Magnetic Lignosulfonate-Supported Pd Complex: Renewable Resource-Derived Catalyst for Aqueous Suzuki–Miyaura Reaction

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ABSTRACT: A novel strategy is described to prepare magnetic Pd nanocatalyst by conjugating lignin with Fe₃O₄ nanoparticles via activation of calcium lignosulfonate, followed by combination with Fe₃O₄ nanoparticles. Tethering 5-amino-1H-tetrazole to calcium lignosulfonate-magnetite hybrid through 3-chloropropyl triethoxysilane enabled coordination of Pd salt with Fe₃O₄-lignosulfonate@5-amino-1H-tetrazole. The underlying changes of the lignosulfonate are identified, and the structural morphology of attained Fe₃O₄-lignosulfonate@5-amino-1H-tetrazole-Pd(II) (FLA-Pd) is characterized by Fourier transform infrared, thermogravimetry differential thermal analysis, energy-dispersive spectrometry, field-emission scanning electron microscopy, transmission electron microscopy, and vibrating sample magnetometer (VSM). The synthesized FLA-Pd displayed high activity for phosphine-free C(sp²)–C(sp²) coupling in water, and the catalyst could be reused for seven successive cycles.

INTRODUCTION

Lignin is an amorphous polymer that comprise three main monomer blocks, namely coniferyl, p-coumaryl, and sinapyl alcohol, and is the second most plentiful biomass on the planet earth after cellulose. One of the most important sources of commercial lignin is the byproduct from biorefineries and pulp industries, and its conversion to a high value-added products has been continually explored. Because of the attendance of phenolic, hydroxyl, methoxy, carbonyl, carboxyl, and aldehyde groups, lignin and its derivatives are endowed with exclusive uses such as antioxidants, antimicrobial agents, in removal of heavy metal ions and toxic dyes, carbon precursors, UV adsorbents, and biomaterials for gene therapy and tissue engineering. Progressive lignin modification has created various functional lignin-based materials with unique properties.

The preparation of heterogeneous catalysts has been extensively investigated in contrast to homogeneous counterparts because of recyclability, facile work-up, and ease of handling. Among heterogeneous catalysts, magnetite nanoparticles (MNP)s have garnered abundant attention owing to their low cost, stability and toxicity, high reactivity, good biocompatibility, easy separation by an external magnet, and importantly, the small size, large surface area, and good magnetic permeability.

The C–C coupling reactions like Sonogashira, Suzuki–Miyaura, Hiyama, and Heck represent strong synthetic tools to generate new natural products, heterocycles, molecular electronics, dendrimers, and conjugated polymers. Among these, Suzuki–Miyaura coupling reactions offer an effective process for the preparation of pharmaceuticals because of compatibility of functional groups and accessibility of organoboron compounds under mild reaction conditions; Pd-catalyzed C–C coupling reactions are one of the most important advancements in synthetic organic chemistry due to high production yields, fast reaction rates, high turnover frequency, and selectivity.

We envisioned an efficient method for the fabrication of the Pd(II) complex supported on Fe₃O₄-lignosulfonate (FLA-Pd) (Scheme 1) and demonstrate its prowess for the phosphine-free Suzuki–Miyaura reaction (Scheme 2) in water as a non-toxic solvent wherein lignin biopolymer, a renewable resource, functions as a natural support for the immobilization of Pd complex.

RESULTS AND DISCUSSION

FLA-Pd Characterization. The characterization of the FLA-Pd was carried out using X-ray diffraction (XRD), transmission electron microscopy (TEM), field-emission scanning electron microscopy (FESEM), energy-dispersive spectrometry (EDS), Fourier transform infrared (FT-IR), vibrating sample magnetometer (VSM), and thermogravimetry differential thermal analysis (TG-DTA) techniques. An XRD pattern of the prepared FLA-Pd was applied for lignosulfonate adsorption on the Fe₃O₄ surface (Figure 1).

The XRD pattern of FLA-Pd was very similar to that of the magnetic NPs, implying that the crystal Fe₃O₄ did not change, and magnetic NPs have been coated with lignosulfonate. The patterns at 2θ values 28.6°, 35.8°, 50.4°, 57.6°, and 63.1° can be attributed to (2 2 0), (3 1 1), (4 2 2), (5 1 1), and...
(4 4 0) planes of the cubic structure of Fe₃O₄ (JCPDS 19-0629), demonstrating the crystalline structure of Fe₃O₄. In addition, the presence of palladium and its immobilization on the Fe₃O₄-lignosulfonate@5-amino-1H-tetrazole was confirmed with the
The peaks at 2800–3000 and 1400–1500 cm$^{-1}$ may be assigned to C–H stretching and bending vibrations of CH$_2$ groups (Figure 2C). Finally, the band around 1450 cm$^{-1}$ indicated the N═N stretching vibrations of the 5-amino-1H-tetrazole (Figure 2D,E).

The chemical composition of calcium lignosulfonate, Fe$_3$O$_4$-lignosulfonate, and the FLA-Pd was analyzed at each stage by the EDS analysis (Figure 3), which confirms the existence of the desired elements in their chemical structure; the EDS spectrum of the lignosulfonate confirmed that it comprised S, C, O, and Ca (Figure 3A). Figure 3 confirmed that C, O, S, Fe, and Ca were main components present in both Fe$_3$O$_4$-lignosulfonate and FLA-Pd along with N, Si, Pd, Cl, K, and I elements, which were present only in the FLA-Pd (Figure 3C), further reaffirming the formation of the final catalyst. Additionally, the existence of C, N, O, Fe, and Pd was emphasized with elemental mapping images (Figure 4), which showed that Pd is dispersed uniformly on the FLA surface.

FESEM images of calcium lignosulfonate, Fe$_3$O$_4$-lignosulfonate, and the FLA-Pd are presented in Figure 5. According to the FESEM analysis results, the shapes of the calcium lignosulfonate are irregular (Figure 5A), while Fe$_3$O$_4$-lignosulfonate has a spherical morphology (Figure 5B). Also, the FLA-Pd show an average particle size in the 20–27 nm range with a spherical morphology. The morphology of the FLA-Pd was also investigated using TEM images (Figure 6), which corroborates FESEM findings.

The results of TG-DTA analysis of FLA-Pd are shown in Figure 7. There are six clear weight loss peaks discernible in the TG-DTA curves. The first weight loss, in the range 30–200 °C, was caused by the elimination of physically absorbed H$_2$O within the Ca lignosulfonate and desorption of organic solvents. The second loss occurred in range 200–290 °C, which is attributed to the cleavage of C═O–C and C–C chemical bonds and other organic moieties. The next weight loss in 300 is due to the decomposition of the calcium lignosulfonate framework, which was associated with the release of small molecules including oxygen, calcium, carbon, sulfur, and hydrogen. The fourth stage, in 400 °C range, corresponds to the disintegration of 5-amino-1H-tetrazole monohydrate. Further, a weight loss was detected in 600 °C, which is caused by the carbonization and decomposition of calcium lignosulfonate and its aromatic rings. The last stage was found in 800 °C, attributed to decomposition of the nanocatalyst.

The magnetic hysteresis loop of the FLA-Pd is illustrated in Figure 8; a magnetic behavior was investigated with the field sweeping in the range of −15 000 to +15 000 Oe. The results acknowledge that the FLA possessed sensitive magnetic responsiveness, which can be easily removed by deploying an external magnet.

**FLA-Pd-Catalyzed Suzuki–Miyaura Reaction.** The catalytic applicability of the FLA-Pd was examined for the Suzuki–Miyaura reaction of iodobenzene with C$_6$H$_5$B(OH)$_2$ as a model reaction. The reaction was carried out deploying 0.05 g of the FLA-Pd and 2.0 mmol of K$_2$CO$_3$ under reflux conditions in H$_2$O as a green solvent; the absence of the FLA-Pd did not produce any coupling reaction, and no coupling product could be observed.

To optimize the catalytic reaction conditions of the PhI (1.0 mmol) with PhB(OH)$_2$ (1.1 mmol) using FLA-Pd, various bases such as K$_2$CO$_3$, NaOAc, NaHCO$_3$, n-Pr$_3$N, Et$_3$N, and solvents namely tetrahydrofuran (THF), toluene, H$_2$O, and EtOH were screened (Table 1); high yield of the favorable
product was discerned when the reaction was performed in water using FLA-Pd (0.05 g) and K2CO3 (2.0 mmol) at 100 °C for 1 h (entry 1).

The reaction between PhB(OH)2 and aryl halides bearing electron-donating and electron-withdrawing groups was performed, and they all afforded biphenyl derivatives in 81–93% yields within 1–2 h using 0.05 g of the FLA-Pd in H2O (Table 2); chlorobenzene produced the corresponding product in good yield as well (entry 13). The melting points of all of biaryls were consistent with the recorded literature values.

Furthermore, we checked the catalytic superiority and remarkable features of FLA-Pd in comparison to reported catalytic systems in the literature for Suzuki–Miyaura reaction in H2O or H2O/EtOH and H2O/DMF mixture (Table 3). Clearly, the
FLA-Pd provided higher yields in a shorter reaction time and higher catalytic activity in comparison to other catalysts.

Catalyst Recyclability. The recyclability of the catalyst system is one of the prominent issues from the standpoint of cost-effectiveness and environmental impact. The FLA-Pd nanocatalyst could be collected via an external magnet because of its magnetic properties. The recyclability of the as-prepared FLA-Pd was next examined using the Suzuki coupling reaction of PhB(OH)2 with PhI in the presence of K2CO3 under reflux conditions in water. As shown in Figure 9, the FLA-Pd can be preserved after two cycles involving the coupling reaction of PhB(OH)2 with PhI. The TEM images of the FLA-Pd catalysts (Figure 6) suggest that the catalyst is well dispersed in the reaction medium. In addition, the TG-DTA analysis in Figure 7 shows that the catalyst is stable up to 200 °C, indicating its potential for practical applications.

Table 1. Preparation of Biphenyl under Different Conditions\(^a\)

| entry | solvent | FLA-Pd (g) | base   | T (°C) | time (min) | yield (%) |
|-------|---------|------------|--------|--------|------------|-----------|
| 1     | THF     | 0.05       | K2CO3  | reflux | 120        | 65        |
| 2     | toluene | 0.05       | K2CO3  | reflux | 120        | 42        |
| 3     | H2O     | 0.05       | —       | rt     | 240        | 0         |
| 4     | H2O     | 0.05       | —       | reflux | 240        | 0         |
| 5     | EtOH    | 0.05       | K2CO3  | reflux | 60         | 70        |
| 6     | H2O     | 0.05       | K2CO3  | reflux | 60         | 93        |
| 7     | H2O     | 0.05       | NaOAc  | reflux | 120        | 50        |
| 8     | H2O     | 0.05       | NaHCO3 | reflux | 120        | 76        |
| 9     | H2O     | 0.05       | Et3N   | reflux | 120        | 61        |
| 10    | H2O     | 0.05       | n-Pr3N | reflux | 120        | 62        |
| 11    | H2O     | 0.03       | K2CO3  | reflux | 120        | 70        |
| 12    | H2O     | 0.07       | K2CO3  | reflux | 60         | 93        |

\(^a\)Reaction conditions: PhI (1.0 mmol); PhB(OH)2 (1.1 mmol); base (2.0 mmol); solvent (10.0 mL). \(^b\)Isolated yield of the pure product.
reused at least seven times, with minor fluctuation in yields. As shown in the TEM and FESEM images of the recycled FLA-Pd (Figures S1 and S2), no clear variation in the morphology of the FLA-Pd and its size was discerned.

**CONCLUSIONS**

This study introduces a new, efficient, and eco-friendly approach for Suzuki–Miyaura coupling reaction through the fabrication of a highly active and sustainable catalytic system using a calcium lignosulfonate biopolymer as a renewable resource and natural support for the immobilization of the 5-amino-1H-tetrazole-Pd(II) complex. The Suzuki–Miyaura coupling reaction was performed for an assorted array of aryl halides in H2O as a greener solvent, and consistently high yields of the biaryls were obtained. In addition, the synthesized catalyst could be reused for successive seven cycles with high efficiency. The use of renewable and abundant resource materials bodes well for its application in other heterogeneous catalytic systems.

**EXPERIMENTAL SECTION**

Reagents and Methods. All chemicals were purchased from Aldrich Chemical Co. and were directly used for the fabrication of catalyst and biaryls. FT-IR spectra using a Thermo Nicolet 370 FT-IR spectrometer were used to record the functional groups in the 400–4000 cm⁻¹ range. TEM and FESEM analyses were used to determine the particle size and morphology using Philips CM120 and Cam scan Mv2300, respectively. The chemical composition analysis of the FLA-Pd was performed using EDS in the FESEM system. XRD analysis was obtained by using a Philips PW 1373 X-ray diffractometer (Cu Kα = 1.5406 Å) in a 2θ range 10°–80° to evaluate the structure of the FLA-Pd. TG-DTG and VSM measurements were performed by using a STA 1500 Rheometric Scientific (England) and Quantum Design MPMS SXL SQUID magnetometer, respectively.

**Preparation of Fe3O4-Lignosulfonate.** For the synthesis of Fe3O4-lignosulfonate, calcium lignosulfonate was activated with potassium periodate (KIO₄) as its functional groups (CHO, OMe, PhOH, and OH) are occupied in interunit linkages; functional group activation help assist its binding to

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Table 2. FLA-Pd-Catalyzed Suzuki–Miyaura Coupling Reaction of C₆H₅BH(OH)₂ with Various Aryl Halides[^25]  

| entry | R | X | time (min) | yield (%)  
|-------|---|---|------------|-------------  
| 1     | H | I | 60         | 93           
| 2     | 4-OMe | I | 60         | 92           
| 3     | 2-OMe | I | 60         | 90           
| 4     | 4-Me | I | 60         | 91           
| 5     | 4-CHO | I | 60         | 90           
| 6     | 4-NO₂ | I | 70         | 90           
| 7     | 4-COOH | I | 60         | 89           
| 8     | H | Br | 90         | 90           
| 9     | 4-OMe | Br | 90         | 89           
| 10    | 4-Me | Br | 90         | 88           
| 11    | 4-NO₂ | Br | 100       | 88           
| 12    | 4-COOH | Br | 90         | 87           
| 13    | H | Cl | 240       | 81           

[^25]: Reaction conditions: C₆H₅BH(OH)₂ (1.1 mmol), aryl halide (1.0 mmol), FLA-Pd (0.05 g), K₂CO₃ (2.0 mmol), H₂O (10.0 mL), reflux. Isolated yield.

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Table 3. Comparison of the FLA-Pd with Other Reported Catalysts in the Reaction of Bromobenzene with C₆H₅BH(OH)₂[^26]  

| entry | catalyst | solvent | T (°C) | time (h) | yield (%)[^27] | ref  
|-------|----------|---------|--------|----------|--------------|------  
| 1     | Pd@Nf-G  | EtOH/H₂O| 80     | 3        | 88           | 31    
| 2     | Pd@aminoclay | H₂O  | 100    | 4        | 87           | 32    
| 3     | Pd NPs/PS | H₂O/DMF| 100    | 12       | 80           | 33    
| 4     | Pd NPs   | H₂O    | 100    | 12       | 85           | 34    
| 5     | Fe₃O₄@RGO@Au@C | H₂O | 100    | 18       | 88           | 35    
| 6     | Au NPs@HS-G-PMS hybrid | H₂O | 110    | 6        | 86           | 36    
| 7     | Fe₃O₄@SiO₂-4-AMTT-Pd(II) | H₂O | 50     | 3.5      | 68           | 37    
| 8     | Pd(OAc)₂/Li | H₂O | 90     | 2        | 86           | 38    
| 9     | Mag-IL-Pd | H₂O    | 60     | 7.5      | 82           | 39    
| 10    | Pd(OAc)₂ | H₂O    | 100    | 12       | 42           | 40    
| 11    | Pd(0)-MCM-41 | EtOH/H₂O | 80     | 12       | 90           | 41    
| 12    | CuO/Pd-3 | DMF    | 110    | 10       | 80           | 42    
| 13    | Pd–CoFe₂O₄ MNP | EtOH | reflex | 12       | 79           | 43    
| 14    | Pd–sepilite | DMF | 100    | 1        | 81           | 44    
| 15    | Ni/Pd core/shell NPs/graphene | DMF/H₂O | 110 | 30 min | 78           | 45    
| 16    | Pd NPs/ionic polymer-doped graphene | EtOH/H₂O | 60     | 24       | 24           | 46    
| 17    | Pd–Co (1:1)/graphene | EtOH/H₂O | 80     | 4        | 76[^28]    | 47    
| 18    | FLA-Pd   | H₂O    | 100    | 1        | 90           | this work |

[^26]: Reaction conditions: C₆H₅BH(OH)₂ (1.1 mmol), aryl halide (1.0 mmol), FLA-Pd (0.05 g), K₂CO₃ (2.0 mmol), H₂O (10.0 mL), reflux. Isolated yield.  

[^27]: Conversion.
the surface of Fe₃O₄. Calcium lignosulfonate was dissolved in the dioxane/water (9:1, v/v) (solution 1) to which aqueous solution of potassium periodate (solution 2) was added in the dark; solution 2 was added with a peristaltic pump into solution 1. Then, Fe₃O₄ nanoparticles (NPs) were added to the preactivated calcium lignosulfonate at pH = 6.4, in mass ratios 5:1 for 2 h. The final solution was filtered, and the ensuing Fe₃O₄-lignosulfonate was washed with EtOH and dried at 110 °C (Scheme 2A).

Preparation of Fe₃O₄@Lignosulfonate@5-Amino-1H-1,2,3-triazole. Fe₃O₄@lignosulfonate@5-amino-1H-1,2,3-triazole (FLA) was obtained by adding (3-chloropropyl)trimethoxysilane (3.0 mL) to 1.0 g Fe₃O₄-lignosulfonate taken in dry toluene (80.0 mL) under reflux conditions and a nitrogen atmosphere for 12 h (Scheme 2B). The synthesized Fe₃O₄-lignosulfonate@(CH₂)₃−Cl was decanted via a magnet, washed with diethyl ether, and then dried under vacuum at 70 °C for 5 h. Next, 5.0 mmol of 5-amino-1H-triazole, 2.0 g of the Fe₃O₄-lignosulfonate@(CH₂)₃−Cl 5.0 mmol of K₂CO₃, and 50.0 mL of DMF were admixed in a flask and refluxed for 24 h. The ensuing Fe₃O₄-lignosulfonate@(CH₂)₃−Cl can be easily collected and used for the next stage (Scheme 2C).

Preparation of the FLA-Pd Complex. Finally, the Fe₃O₄-lignosulfonate@(CH₂)₃−Cl (1.0) and 0.5 g of PdCl₂ were mixed in EtOH (50.0 mL) and heated at 80 °C for 24 h. Then, the obtained complex was collected with an external magnet, washed with EtOH, dried, and then used as a new magnetic catalyst in the next cycle (Scheme 2D).

Suzuki−Miyaura Coupling Reaction. A round-bottomed flask was filled with 1.1 mmol of C₆H₅B(OH)₂, 1.0 mmol of aryl halide, 2.0 mmol of K₂CO₃, 0.05 g of FLA-Pd, and 10 mL of water and stirred under reflux conditions for the adequate time. The conversion of aryl halide was checked by thin-layer chromatography. When the reaction was completed, the catalyst was decanted using an external magnetic field, and the coupling product was then purified by flash chromatography. The obtained biaryls were characterized by melting point and conformation by NMR.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01640.

NMR and FESEM images for the recovered FLA-Pd catalyst (PDF)

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Notes

The authors declare no competing financial interest.

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