Deposition of Palladium Nanoparticles by the Coating of the Carbonaceous Layer from Wastepaper-Derived Bio-Oil

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ABSTRACT: A highly active and recyclable Pd-deposited catalyst has been successfully prepared for the Heck reaction. Bio-oil liquid, a byproduct from the microwave pyrolysis of wastepaper, is employed to immobilize palladium nanoparticles on a solid support. FTIR, GC, and NMR results indicate the self-polymerization feature of bio-oil, thus giving rise to a uniform carbonaceous layer coated around the surface of the catalyst. Characteristic analysis of the catalyst indicates that palladium nanoparticles are well-dispersed on the parent SBA-15 solid substrate, which is attributed to the carbonaceous layer that is derived from bio-oil carbonization, allowing a high catalytic performance as a heterogeneous catalyst for the Heck reaction. The as-synthesized catalyst demonstrates remarkable recyclability with firm deposition of palladium nanoparticles on the solid support and could be reused without a dramatic decrease in catalytic activity.

1. INTRODUCTION

The conversion of waste materials, such as waste office paper and biomass, into high valuable products can mitigate a variety of serious socioeconomic problems.1 Although recycling of waste office paper has huge environmental and economic benefits, it cannot be recycled indefinitely due to the weak fiber structure,2 thus impeding the development of the used paper recovery. On the other hand, due to the direct incineration or landfill of wastepaper, negative environmental and regulation impacts will be subsequently arisen. In recent years, innovative approaches regarding wastepaper valorization have been increasingly developed as an alternative of high valuable purified chemicals.3,4 Notably, our previous investigation demonstrated that waste office paper can be converted into value-added products via a microwave-involved pyrolysis process.5 Among the pyrolysis products, the cheap, biodegradable, and abundant bio-oil has been impressively attractive as a substituted energy source or a feedstock for chemical production.5–8 This is technically feasible but with high energetic and financial cost to obtain purified compounds from the bio-oil or upgrade bio-oil for producing a commercial fuel.9 In this work, without any pretreatment, bio-oil will be directly utilized as a biodegradable and cost-effective carbon source for silica surface modification and palladium nanoparticle (PdNP) deposition.

Palladium-catalyzed coupling reactions are of great importance in organic synthesis since C–C bond construction contributes to the binding of different molecules. For instance, the Heck reaction is a C–C coupling reaction of an unsaturated halide with an alkene in a base and a palladium catalyst to generate a substituted alkene.10,11 Nevertheless, the recovery and reuse of the palladium-based catalysts are still challenging since its first discovery in the 1970s. Great efforts on improving the elemental sustainability have been devoted.12–15 Heterogeneous catalysts composed of Pd species and a solid support possess advantages of recyclability, reusability, and simple separation from the reaction system.16–19 The physical and chemical nature of the solid support will have a substantial impact on catalyst performance during the reaction: the deposition of PdNPs by the pore channels of the substrate dramatically prevents the deactivation of the metal nanoparticles.20 Due to chemical inertness under moderate experimental conditions, carbonaceous materials have been applied as the solid support for C–C coupling reactions and hydrogenation.21 The incorporation of silica species can address broad pore size distribution and structural shrinkage of the carbonaceous materials.22 Here in our work, a thin carbonaceous layer, generated by the carbonization of wastepaper-derived bio-oil, is firmly and uniformly coated on the surface of the solid support for the deposition of PdNPs.

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2. RESULTS AND DISCUSSION

2.1. Production and Characterization of Bio-Oil from Microwave Pyrolysis of Wastepaper. Paper and paperboard derived from wood pulp contain cellulose, hemicellulose, lignin, and small amounts of mineral materials, where cellulose is the predominant component. After the pyrolysis with a programmed increase in temperature, bio-oils are produced through the depolymerization and fragmentation of the polysaccharides (cellulose, hemicellulose, and lignin). It should be noted that owing to shorter operation times, high efficiency, and controllability of the process, a microwave technique is employed for our wastepaper pyrolysis.23 The surface of the wastepaper will be penetrated by microwaves, resulting in a uniform heating both on the surface and interior of the material. As a result, the bio-oil was produced and subsequently used for further catalyst preparation.24

As indicated in the GC spectra of the bio-oil (in Figure S2), it is clearly shown that the bio-oil contains complex organic compounds, and the major components of the bio-oil could be categorized into three different classes: saccharide derivatives, furanic compounds, and aromatics. $^1$H NMR and $^{13}$C NMR (Figure 1A,B) spectra are illustrated in Figure 1A,B. Major identified functional groups like aromatics, aliphatics, alcohols, and olefins are illustrated in the spectra. Intensive signals in the aliphatic range indicate that there are significant percentages of the aliphatic groups in the bio-oil, which derives from long-chain fatty acids or alkyl groups.25 The aromatic functional groups are confirmed by the peaks at 6−8 ppm in the $^1$H spectra and 110−150 ppm in the $^{13}$C spectra.26 In addition, the peaks at 3−4 ppm in the $^1$H spectra are also likely attributed to the proton signal that is adjacent to C−O groups and aromatic bridging methylene groups. The signals at 50−100 ppm shown in Figure 1B are ascribed to the carbon atoms adjacent to oxygenated groups, indicative of the presence of the sugar-derived compounds.27 It could be concluded that in the bio-oils, the carbohydrates and their derivatives are the predominant compositions, along with a relatively low proportion of the aromatic compounds. These compounds containing unsaturated bonds may induce a polymerization process on the surface silica species during the heating to immobilize the palladium nanoparticles.

Figure 1C shows the FTIR result, and the major peaks are identified and listed in Figure 1D. The assigned peaks in the spectra match well with the GC and NMR results: the aliphatic group is evidenced by the peak at 2850−3000 cm$^{-1}$, which is attributed to the −CH stretching vibrations; the peak observed at ~1053 cm$^{-1}$ is attributed to the C−O−C vibration from the pyranose structure, suggesting the presence of polysaccharides.

Figure 1. (A) $^1$H and (B) $^{13}$C NMR spectra of the bio-oil; (C) FTIR spectra, and (D) major identified peaks for FTIR spectra.
Other oxygenated functional groups including C═O and O—H induce the peaks at 1724 and 3300 cm\(^{-1}\), respectively.\(^{25,28,29}\) The oxygenated compounds are beneficial for the generation of uniform carbonaceous layers, as they will promote strong interactions with residual silanol groups in the silica support to form a rigid coating around inside of the SBA-15 pores. In addition, the aromatics in the bio-oil are confirmed by the peak at 1610 cm\(^{-1}\), which is assigned to C═C stretching vibrations.\(^{30}\) A previous study revealed that since aldehyde may undergo aldol condensation and double bonds can self-polymerize, the physical and chemical properties of the bio-oil change gently.\(^{30}\) For monitoring the compositional change of the liquid oil, it is analyzed by FTIR after being stored for different periods.

Figure 2. Schematic process of the P-1 catalyst for the Heck reaction.

Figure 3. (A) N\(_2\) adsorption/desorption isotherm plots and (B) pore size distributions of the samples (inset graph: parent SBA-15); (C) TEM images of the P-1 and P-2 samples; (D) Pd3d XPS spectra of the P-1 sample.
chemical composition in the bio-oil did not change dramatically.

The thermogravimetric analysis (see Figure S3) demonstrates that bio-oil has a mass loss of approximately 80% at 500 °C. The light volatile evaporation results in a mass loss accompanied by a minor peak at 150 °C. Another peak in the DTG plot is observed at 230 °C with a weight loss of ~48%, which is likely attributed to the decomposition of polysaccharides. The residual mass is approximately 21.49% at 500 °C, and the solid carbonaceous materials are generated. In this work, the temperature for the preparation of P-1 material is kept at 500 °C.

Instead of a conventional carbon source, which is toxic, materials that either compete with food or is highly purified are used,\textsuperscript{31,32} there are numerous renewable and low-cost feedstocks that can be utilized for preparing carbon-based materials, such as raw biomasses, raw coals, and sawdusts.\textsuperscript{3,33,34} However, those feedstocks in solid form hardly control the pore network of the resulting carbon products. The bio-oil from microwave pyrolysis of wastepaper can address this issue and thus is employed as a biodegradable and cost-effective carbon source. GC, NMR, and FTIR results comprehensively indicate the complex composition of oxygenated compounds, giving rise to the unique self-polymerization feature of bio-oil. The unsaturated functional groups will be condensed and polymerized under heating, and the liquid bio-oil will result in a solid carbonaceous form. Moreover, it has been reported that these oxygenated groups will have a high reactivity with unhydrated silanol groups in silica supports; the part of bio-oil that is attached to the surface of SBA-15 will be much easier to interact with each other. The C\textsubscript{1s} XPS analysis of the P-1 sample shows that the C–O–Si bond is observed (shown in Figure S4), supporting that the carbonaceous layer is successfully coated on the surface of the silica material. As a result, a carbonaceous layer will be eventually formed on the surface of the SBA-15 substrate.\textsuperscript{35} As such, the PdNPs will be anchored by the carbonaceous layer, minimizing the leaching of the metal and improving the reusability and recoverability.

As illustrated in Figure 2, the bio-oil derived from waste office paper is carbonized at 500 °C and subsequently coated to the surface of the silica substrate for the fabrication of a novel heterogeneous catalyst for the Heck reaction. Thanks to the incorporation of bio-oil, the carbonaceous layer not only gives a solid carbonaceous form. Moreover, it has been reported that these oxygenated groups will have a high reactivity with unhydrated silanol groups in silica supports; the part of bio-oil that is attached to the surface of SBA-15 will be much easier to interact with each other. The C\textsubscript{1s} XPS analysis of the P-1 sample shows that the C–O–Si bond is observed (shown in Figure S4), supporting that the carbonaceous layer is successfully coated on the surface of the silica material. As a result, a carbonaceous layer will be eventually formed on the surface of the SBA-15 substrate.\textsuperscript{35} As such, the PdNPs will be anchored by the carbonaceous layer, minimizing the leaching of the metal and improving the reusability and recoverability.

As illustrated in Figure 2, the bio-oil derived from waste office paper is carbonized at 500 °C and subsequently coated to the surface of the silica substrate for the fabrication of a novel heterogeneous catalyst for the Heck reaction. Thanks to the incorporation of bio-oil, the carbonaceous layer not only gives rise to well-dispersive and uniform PdNPs on the surface of solid supports that increase the active sites and promote the catalytic efficiency but also enables the firm anchoring of PdNPs onto the surface of the solid support and avoids the metal leaching into the reaction solution and consequent product contamination. Hence, the reuse and recovery of the as-synthesized heterogeneous catalyst are significantly enhanced in comparison to other catalysts (P-2 and P-3). In addition, it is also noted that the carbonaceous layer is generated from bio-oil that is renewable and cost-effective. This versatile metal deposition strategy is realized by the incorporation of bio-oil as a carbonaceous layer and may find a high valuable and innovative application for bioresource-derived products, promoting to a more sustainable chemistry.

### 2.2. Textural Properties of Catalyst Samples

The P-1 and P-2 catalysts are fabricated following the Experimental section, and the P-3 sample is directly purchased from a commercial supplier and used without further treatments. Prior to investigating their catalytic performances in the Heck reaction, the textural properties and crystalline structures are characterized. With a typical Type IV isotherm observed from the adsorption/desorption isotherm plot of the P-1 catalyst (Figure 3A), its mesostructure feature is confirmed. Notably, different from the parent SBA-15 sample (shown in Figure S5), the H2-type hysteresis loop at a relative pressure of 0.4–0.8 displays a gradual rise in the adsorption branch of the P-1 catalyst during capillary condensation, revealing a pore structure with an ink-bottle model. This is due to the incorporation of the carbonaceous layer onto the surface of the silica substrate, resulting in a less uniformity of the pore structure.\textsuperscript{36} Given that the oxygenated groups in bio-oils are highly reactive with unhydrated silanol groups in silica species, a thin carbonaceous layer will therefore be formed by coating around the pore wall of the SBA-15 substrate, along with the entrapment of PdNPs. This can be evidenced by the XPS result in Figure S4, showing the existence of the C–O–Si bond. Nonetheless, the incorporation of bio-oil will result in a reduction in the pore volume and the specific surface area of the P-1 catalyst, compared to the P-2 catalyst and the parent SBA-15 sample. Two significant drop steps observed in the desorption branch of the P-2 catalyst indicate two pore size distributions, which could also be reflected from pore size distribution in Figure 3B. This is due to the aggregation of PdNPs in the P-2 sample, as reflected in TEM images (Figure 3C). The pore-size distribution plot of the P-1 catalyst displays one peak centered at 3.8 nm, suggesting that the metallic PdNPs are well-dispersed on the solid support. On the other hand, in the Figure 3B inset, the SBA-15 sample has an average pore size of 6.5 nm. Hence, based on the pore size of the P-1 and parent SBA-15 samples, the estimated thickness of the carbonaceous layer is calculated to be ca. 2.7 nm. The textural properties of the as-synthesized catalyst are illustrated in Table 1. The XPS results of the duplicated P-1 samples reveal that the Pd content is ~8.9 w/w. %, indicating that the palladium nanoparticles are evenly distributed on the carbon–silica substrate. It should be noted that the Pd content obtained from XPS analysis is slightly higher than the calculated value of 7.7%, which could be explained by the surface sensitivity of XPS technique.\textsuperscript{35} The surface of the catalyst is enriched with a Pd-containing carbon layer due to the coating of carbon species around the walls of the silica support. The oxidation state of Pd can also be identified by deconvolution of the assigned peak, as shown in Figure 3D. The binding energy peaks at 342.2 eV (Pd 3d3) and 336.9 eV (Pd 3d5) are attributed to the Pd(II); meanwhile, the binding energy peaks at 340.2 eV (Pd 3d3) and 335.0 eV (Pd 3d5) are the characteristics of the Pd(0) species, which are the active species of Pd for catalyzing the reaction.\textsuperscript{18} Calculated from the deconvoluted XPS curve, the ratio of Pd(0) and Pd(II) is estimated to be 4:1. In addition, the isotherm plot and pore size distribution of a commercial P-3 catalyst demonstrate a typical meso- and micro-porous carbon material with nonuni-

| Table 1. Textural Properties of the As-Synthesized Materials |
|------------------------------------------|
| sample | BET surface area (m\textsuperscript{2} g\textsuperscript{-1}) | t-plot micropore area (m\textsuperscript{2} g\textsuperscript{-1}) | pore volume (cm\textsuperscript{3} g\textsuperscript{-1}) | pore diameter (nm) |
| P-1 | 355 | 193 | 0.13 | 3.3 |
| P-2 | 408 | 121 | 0.53 | 4.7 |
| P-3 | 844 | 483 | 0.41 | 5.1 |
| SBA-15 | 732 | 186 | 0.80 | 5.1 |

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form pore sizes. The results support that the mesostructures and ample mesopores in the P-1 catalyst are inherited from the parent SBA-15 material after the incorporation of PdNPs and the carbonaceous layer, therefore giving rise to a high flow ability of the liquid phase when initiating the Heck reaction. TEM images in Figure 3C intuitively show that the PdNPs are well-dispersed on the carbon—silica substrate, whereas there are PdNPs aggregated on the surface of the silica substrate (green circle in Figure 3C). The abovementioned self-polymerization feature of bio-oil prevents the PdNPs from aggregating during the carbonization, thus hindering the catalytic activity of the sample, further allowing the P-1 sample to be more effective in catalyzing the Heck reaction than other catalysts. Proved by a previous study, the abundant hydroxyl groups on the surface of the solid support material were conjugated with metal nanoparticles, which is also beneficial for obtaining detached and well-dispersed PdNPs.16 The signals observed in the small-angle XRD results of both P-1 and P-2 samples (Figure 4A) indicate that these two samples possess the ordered hexagonal lattice. There is one 100 diffraction peak at 0.98° for the P-2 sample, supporting that the catalyst has the mesostructure feature after the palladium deposition,37 potentially allowing for a better fluid flow performance. Compared to that of the P-2 sample, the peak position of the P-1 sample shifting from 0.98 to 1.0° demonstrates that this sample possesses a smaller interplanar distance d100 space, resulting from the silica framework shrinkage after the high-temperature heating treatment. Clearly, no significant peak could be seen in the pattern of the P-3 sample due to a disordered porous structure. Figure 4B clearly shows the dominant peaks at 2θ = 40°, 46°, and 68°, which belong to the characteristic peak of the face-centred cubic (fcc) Pd lattice.38 This result suggests the successful incorporation of PdNPs into the solid supports. Notably, the amorphous carbon/amorphous silica structure may contribute to the signal centered at 23°. In addition, the XRD pattern of the aluminum sample holder is displayed in Figure S6, corresponding to the asterisk signal.

2.3. Catalytic Activity of the Catalyst. The catalytic performance of the P-1 catalyst is studied by catalyzing the Heck reaction (Figure 5A). The proposed mechanism has been well acknowledged, and the catalytic cycle is plotted in Figure S7. Recycling and reuse of the P-1 sample are undertaken by filtrating the catalyst from the reaction media and transferring it to a new reaction without an additional activation process. N-methylpyrrolidone (NMP) is utilized for the reaction, and the results (Figure 5B) indicate that the catalyst could only be reused 4 times. There is a significant drop of conversion (28%) for the fifth use and further decreases to 13% at the sixth run. By the end of the reaction, methyl cinnamate as the primary product is separated from the liquid phase for identification. EI Mass spectra and 1H NMR spectra (see Figure S8) of the purified sample match well with those of the standard methyl cinnamate sample.

Conventionally, N-methylpyrrolidone (NMP) is frequently utilized for the Heck reaction.39 Its high dipolarity feature...
could stabilize the alkene intermediate, thus accelerating the reactions.\textsuperscript{40} Although NMP is functioned properly for the Heck reaction with the as-synthesized P-1 catalyst, there are some environmental and toxic concerns that may impede the use of organic solvents.\textsuperscript{41} A benign organic cyclic carbonate with high dipolarity is proposed by a green chemistry group in the University of York,\textsuperscript{49} as an alternative of conventional organic solvents. The propylene carbonate has a similar dipolarity ($\pi^* = 0.90$) with NMP and thus could also promote a good productivity of the Heck reaction. Although a previous study described the feasibility of propylene carbonate for the Heck reaction, the impacts of this alternative solvent on the reusability and recyclability of the heterogeneous catalysts are not deeply explored.

In Figure 5C, the conversion of the reaction is 96\% at the eighth run for the P-1 catalyst in the presence of PC. Compared with a previous study,\textsuperscript{14,16,20,42,43} the as-synthesized P-1 catalyst has a superior recyclability. A control experiment of purified palladium acetate is carried out under identical conditions and results in a conversion of 89.0\%, but it could hardly be recycled owing to the dissolution of the catalyst in the reaction solvent. Figure 5B and Figure 5C, the results clearly demonstrate that the recyclability of the catalyst in PC is superior to that in NMP. To explore the catalyst activity loss in NMP, a reactivation process is undertaken via re-heating the used sample followed by the addition to a fresh portion of starting reagent. The conversion is significantly raised from 13 to 84\%. It has been revealed that triethylamine hydroiodide (Et$_3$NHI) forms as a byproduct will adsorb on the surface of the catalyst.\textsuperscript{44} Hence, the pores are blocked, and PdNPs are covered by insoluble compounds. Removal of the insoluble compound results in the increase of catalytic ability. This phenomenon exactly suggests that PdNPs are still deposited on the pores of the catalyst, benefiting from the anchoring effect of carbonaceous layers; and the removal of the byproduct will contribute to the recovery of the catalyst. In the case of PC, it is demonstrated that the reusability of the catalyst is superior to that in NMP, likely attributed to the suppression of the Et$_3$NHI production in the PC system, which is in agreement with previous research, observing an enhanced yield and good selectivity in the presence of PC for the Pd-catalyzed reaction.\textsuperscript{35–47}

The effect of the concentration of PdNPs on the reaction conversion rate is also investigated and illustrated in Figure S9. Under identical reaction conditions, the catalytic performance of the high-Pd-loading sample outperforms the sample with a low Pd loading. Impressively, it is worthwhile to note that the conversion of methyl acrylate is 88\% for the 0.04 mol P-1 sample, suggesting the efficiency of the catalyst with an ultralow Pd loading. This could be interpreted by the Pd uniformity, resulting from the polymerization of bio-oil.

Table 2 shows the reaction conversion and selectivity depending on the different reaction runs. The ratio of the production yield to the conversion of the reaction equals the selectivity of the reaction. It is shown that the P-1 sample catalyzes the reaction with a high selectivity of 87\% or higher. The aforementioned discussion in Section 3.2 indicated that the PdNPs are firmly fixed on the substrate. This can be supported by determining the PdNP concentration in the liquid solution after the completion of the reaction. ICP analysis results shown in Table 2 demonstrate that the recycled solution, starting from the second run, contains less than 5 ppm of palladium, and the mass of PdNPs detached from the catalyst is lower than 0.9\%, highlighting the stability of this heterogeneous Pd catalyst, resulting from the stabilizing effect of the carbon–silica support. Attributed to the carbonaceous layer generated from the bio-oil carbonization, the P-1 sample is superior in catalyzing the reaction in terms of the recyclability and conversion rate.

Table 2. Pd Loss, Selectivity, and Conversion of the Heck Reaction

| run number | Pd wt in solution ppm | Pd loss wt % | selectivity % | conversion % |
|-----------|-----------------------|--------------|---------------|--------------|
| 1         | 8.72                  | 1.2          | 96            | 93.5 ± 2     |
| 2         | 2.91                  | 0.3          | 95            | 90 ± 4       |
| 3         | 3.33                  | 0.4          | 87            | 92.5 ± 2     |
| 4         | 4.14                  | 0.5          | 89            | 91.5 ± 3     |
| 5         | 3.12                  | 0.4          | 98            | 88.5 ± 1     |
| 6         | 3.58                  | 0.4          | 97            | 89 ± 1       |
| 7         | 4.98                  | 0.9          | 98            | 93 ± 3       |
| 8         | 4.36                  | 0.5          | 97            | 96 ± 3       |

The catalytic properties and the recyclability performance of the P-1, P-2, and P-3 samples are compared and listed in Figure 6A. Benefiting from the incorporation of bio-oil, the P-1 catalyst has a better catalytic performance for the reaction, as well as reusability. The reaction conversion for the P-2 sample dramatically decreases by 80\% at the third run due to the leaching of PdNPs so that the sample loses its catalytic ability. The commercial P-3 catalyst has a similar situation to the P-2 sample, showing that it could only be reused for 4 runs. Remarkably, the P-1 catalyst shows a better recyclability, compared to other catalyst, and could be reused at least 8 times, resulting from the well-dispersed PdNPs on the material’s surface and the stabilizing effect of the polymerized carbonaceous layer for PdNPs. Meanwhile, a reactivation process of both P-2 and P-3 is initiated by the heating step at
500 °C under a nitrogen flow. The result indicates that there is a limited increase (~2%) in conversion, indicating that the catalyst has deactivated due to the PdNPs leaching from the catalyst. In addition, another control experiment using a bare solid support without loading palladium as the catalyst (including the carbon–silica substrate and SBA-15) is also carried out, and the result suggests that the solid support without PdNP loading could not catalyze this reaction properly.

The feasibility of the as-synthesized catalyst for the Heck reaction is further examined using different types of starting reagents. A range of aryl halides are utilized as a substitution reagent to further investigate the catalytic performance of the catalyst. The P-1 sample shows a comparable or superior catalytic activity over the P-2 and P-3 catalyst when substituted aryl halides are utilized, and the results are listed in Figure 6B (Entry 3, 4, 5, 6, 9). Electron-withdrawing groups tend to advance the Heck reaction rate by decreasing the electron density on the aromatic ring of the halogenated species, and thus when aryl bromide is combined with NO2 and CN density on the aromatic ring of the halogenated species, and advance the Heck reaction rate by decreasing the electron (Entry 3, 4, 5, 6, 9). Electron-withdrawing groups tend to decrease in conversion considerably when the electron-donating groups are introduced (Entry 3, 4, 5). However, aryl chlorides are much less active in the Heck coupling reaction than aryl bromides and aryl iodides so that chlorobenzene is difficult to react with. This is a result of the slow addition rate of C–Cl and Pd(0), which could be explained by the theory that the bond energy between carbon and chlorine is stronger than that between carbon and bromine/iodine.48,49 This leads to a slow conversion (<15%) for the aryl chloride reaction (Entry 1, 2).

3. CONCLUSIONS

The bio-oil is generated from the wastepaper, and its unique properties including self-polymerization feature and interactions with the silica support lead to a thin carbonaceous layer on the surface of silica through the carbonization. This resulting carbonaceous layer could not only give rise to well-dispersive and uniform PdNPs on the surface of solid supports but more importantly enable the firm anchoring of PdNPs onto the solid support. A Pd-deposited catalyst has been successfully prepared in a sustainable and low-cost way and could be reused effectively for the Heck reaction with little Pd leaching (<1.0%) in the presence of PC, in comparison to those baseline catalysts. The strategy of metal deposition using the waste resource-derived bio-oil may advance the development of low-cost and reusable heterogeneous materials for catalysis, separation, and adsorption.

4. MATERIALS AND METHODS

4.1. Bio-Oil Preparation Via Microwave Fast Pyrolysis.

The bio-oil was prepared through the microwave fast pyrolysis of wastepaper using a Milestone ROTO SYNTH rotative solid phase microwave reactor (Milestone Srl, Italy), shown in Figure S1.50 Prior to the pyrolysis, the wastepaper was shredded and pressed into a dense cube. The paper cube was then microwave pyrolyzed at ~200 °C under continuous vacuum. The bio-oil fractions were then condensed and collected with ice under vacuum. The Fourier transform infrared (FTIR) spectra are recorded on a Bruker Vertex 70 spectrometer using an attenuated total reflectance (ATR) technique in the range of 4000–650 cm−1 wavenumbers. NMR spectra were collected on a JEOL JNM-ECS400 MHz spectrometer at 298 K.

4.2. Catalyst Preparation and Characterization. The mesoporous SBA-15 was synthesized in a sol–gel method by following a procedure similar to that designed by Zhao et al.51 Triblock poly(ethylene glycol)–poly(propylene glycol)–poly(ethylene glycol) (P123), deionized water, and 2 M HCl were mixed by magnetic stirring followed by the addition of certain amounts of tetraethyl orthosilicate (TEOS) at 40 °C for 24 h. Then, the sol was aged at 80 °C for 48 h. The white precipitate was then collected by filtration, washed with deionized water and acetone, and dried at 100 °C. Finally, the SBA-15 sample was calcined at 550 °C in air for 6 h to remove excess organic species.

The palladium carbon–silica catalyst (P-1) was synthesized through a wet impregnation process. In a typical synthesis, certain amounts of bio-oil, palladium acetate, and SBA-15 were well-dispersed into acetone by stirring overnight followed by the evaporation of the solvent at 60 °C to obtain a viscous type of liquid. The carbonization process was carried out at 500 °C (heating rate of 1 °C/min) under an inert atmosphere to finally produce the P-1 catalyst. Similarly, the P-2 catalyst was synthesized but without the use of bio-oil liquid. The palladium on the activated carbon support (P-3, 10 wt % Pd loading, 205699, Sigma-Aldrich Co.) was directly purchased and used without any further modification.

For the characterization of the catalysts, transmission electron microscopy (TEM) images were collected using a FEI Tecnai 12 G2 microscope. N2 adsorption was performed at −196 °C using a micropore surface analyzer (ASAP 2020, Micromeritics). The sample degas treatment was completed under vacuum for 4 h at 180 °C. Powder XRD measurements of the samples were carried out using Cu Kα radiation in the 2θ ranges of 0.5–4.0° (small angle) and 10–80 °C (wide angle) on a BRUKER D8 ADVANCE X-ray diffractometer. Inductively coupled plasma (ICP) was collected using an Agilent 7700x. Sample and Skimmer Cones were Ni, and the analysis was run in He mode.

4.3. Heck Reaction Process. In a round-bottom flask equipped with a mechanical stirrer, a mixture of iodobenzene or aryl halides, methyl acrylate, trimethylamine, and solvent was added followed by the catalyst. The mixture was heated at 100 °C by using an oil bath. After the completion of the reaction, the reaction conversion was determined by 1H NMR, and the product yield was monitored by GC–MS. Inductively coupled plasma mass spectrometry (ICP-MS) analysis was performed using an Agilent 7700x. The final product was purified by column chromatography.
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ABBREVIATIONS
NMP, N-methylpyrrolidone; PdNPs, palladium nanoparticles; PC, propylene carbonate

REFERENCES
(1) Joshi, G.; Naithani, S.; Varshney, V. K.; Bisht, S. S.; Rana, V.; Gupta, P. K. Synthesis and characterization of carboxymethyl cellulose from office waste paper: A greener approach towards waste management. Waste. Manag. 2015, 38, 33–40.
(2) Zhang, Z.; Macquarrie, D. J.; De Bruyn, M.; Budarin, V. L.; Hunt, A. J.; Gronnow, M. J.; Fan, J.; Shuttleworth, P. S.; Clark, J. H.; Matharu, A. S. Low-temperature microwave-assisted pyrolysis of waste office paper and the application of bio-oil as an AI adhesive. Green. Chem. 2015, 17, 260–270.
(3) Ikekda, Y.; Park, E. Y.; Okuda, N. Bioconversion of waste office paper to gluconic acid in a turbine blade reactor by the filamentous fungus Aspergillus niger. Bioresour. Technol. 2006, 97, 1030–1035.
(4) Yen, H. W.; Brune, D. E. Anaerobic co-digestion of algal sludge and waste paper to produce methane. Bioresour. Technol. 2007, 98, 130–134.
(5) Jahirul, M. I.; Rasul, M. G.; Chowdhury, A. A.; Ashwath, N. Biofuels production through biomass pyrolysis—a technological review. Energies. 2012, 5, 4952–5001.
(6) Bridgewater, A. V. Review of fast pyrolysis of biomass and product upgrading. Biomass. Bioenergy. 2012, 38, 68–94.
(7) Titirici, M. M.; White, R. J.; Falco, C.; Sevilla, M. Black perspectives for a green future: hydrothermal carbons for environment protection and energy storage. Environ. Environ. Sci. 2012, 5, 6796–6822.
(8) Thompson, E.; Danks, A.; Bourgeois, L.; Schnepfer, Z. Iron-catalyzed graphitization of biomass. Green. Chem. 2015, 17, 551–556.
(9) Yamvuka, D. Bio-oil, solid and gaseous biofuels from biomass pyrolysis processes—An overview. Int. J. Energy. Res. 2011, 35, 835–862.
(10) Bruce, P. Y., Organometallic Compounds. In Organic Chemistry, Zalesky, J., Ed. Prentice Hall: 2011; pp S19–522.
(11) Johansson Seechurn, C. C.; Kitching, M. O.; Colacot, T. J.; Snieckus, V. Palladium-catalyzed cross-coupling: a historical contextual perspective to the 2010 Nobel Prize. Angew. Chem., Int. Ed. 2012, 51, 5062–5085.
(12) Veisi, H.; Faraji, A. R.; Hemmati, S.; Gil, A. Green synthesis of palladium nanoparticles using Pustacia atlantica kurdica gum and their catalytic performance in Mizoroki–Heck and Suzuki–Miyaura coupling reactions in aqueous solutions. Appl. Organomet. Chem. 2015, 29, S17–S23.
(13) Martinez-Klimov, M. E.; Hernandez-Hipolito, P.; Klimova, T. E.; Solis-Casados, D. A.; Martinez-García, M. Development of reusable palladium catalysts supported on hydrogen titane nanotubes for the Heck reaction. J. Catal. 2016, 342, 138–150.
(14) Hajipour, A. R.; Rezaei, F.; Khorsandi, Z. Pd/Cu-free Heck and Sonogashira cross-coupling reaction by Co nanoparticles immobilized on magnetic chitosan as reusable catalyst. Green. Chem. 2017, 19, 1353–1361.
(15) Pourjavadi, A.; Motamed, A.; Marvdashiti, Z.; Hosseini, S. H. Magnetic nanocomposite based on functionalized salep as a green support for immobilization of palladium nanoparticles: Reusable heterogeneous catalyst for Suzuki coupling reactions. Catal. Commun. 2017, 97, 27–31.
(16) Liu, G. H.; Bai, X. F.; Lv, H. F. Green synthesis of supported palladium nanoparticles employing pine needles as reducing agent and carrier: New reusable heterogeneous catalyst in the Suzuki coupling reaction. Appl. Organomet. Chem. 2017, 31, No. 7.
(17) de Clippel, F.; Harkiolakis, A.; Ke, X.; Vosch, T.; Van Tendeloo, G.; Baron, G. V.; Jacobs, P. A.; Denayer, J. F.; Sels, B. F. Molecular sieve properties of mesoporous silica with intraporous nanocarbon. Chem. Commun. 2010, 46, 928–930.
(18) Yu, L.; Huang, Y.; Wei, Z.; Ding, Y.; Su, C.; Xu, Q. Heck Reactions Catalyzed by Ultrasmall and Uniform Pd Nanoparticles Supported on Polyamine. J. Org. Chem. 2015, 80, 8677–8683.
(19) Zhang, D.; Wei, Z.; Yu, L. Easily fabricated and recyclable PdCu/AI catalyst for gram-scale phosphine-free Heck reactions with high TON. Sci. Bull. 2017, 62, 1325–1330.
(20) Taladriz-Blanco, P.; Hervés, P.; Pérez-Juste, J. Supported Pd Nanoparticles for Carbon–Carbon Coupling Reactions. Top. Catal. 2013, 56, 1154–1170.
(21) Guerra, J.; Herrero, M. A. Hybrid materials based on Pd nanoparticles on carbon nanostructures for environmentally benign C-C coupling chemistry. Nanoscale 2010, 2, 1390–1400.
(22) Wang, J.; Xiang, C.; Liu, Q.; Pan, Y.; Guo, J. Ordered Mesoporous Carbon/Fused Silica Composites. Adv. Funct. Mater. 2008, 18, 2995–3002.
(23) Mokhtar, N. M.; Omar, R.; Idris, A. Microwave Pyrolysis for Conversion of Materials to Energy: A Brief Review. Energy. Sources. Part. A 2012, 34, 2104–2122.
(24) Wu, C.; Budarin, V. L.; Gronnow, M. J.; De Bruyn, M.; Onwudili, J. A.; Clark, J. H.; Williams, P. T. Conventional and microwave-assisted pyrolysis of biomass under different heating rates. J. Anal. Appl. Pyrolysis 2014, 107, 276–283.
(25) Demiral, I.; Eryazici, A.; Şensoz, S. Bio-oil production from pyrolysis of corn cob (Zea mays L.). Biomass. Bioenergy. 2012, 36, 43–49.
(26) Morali, U.; Şensoz, S. Pyrolysis of hornbeam shell (Carpinus betulus L.) in a fixed bed reactor: Characterization of bio-oil and biochar. Fuel 2015, 150, 672–678.
(27) Mullen, C. A.; Strahan, G. D.; Boateng, A. A. Characterization of Various Fast-Pyrolysis Bio-Oils by NMR Spectroscopy. Energy. Fuels. 2009, 23, 2707–2718.
(28) Rutkowski, P. Pyrolysis of cellulose, xylan and lignin with the K2CO3 and ZnCl2 addition for bio-oil production. Fuel Process. Technol. 2011, 92, S17–S22.
(29) Pütün, A. E.; Özcan, A.; Pütün, E. Pyrolysis of hazelnut shells in a fixed-bed tubular reactor: yields and structural analysis of bio-oil. J. Anal. Appl. Pyrolysis. 1999, 52, 33–49.
(30) Lu, Q.; Yang, X.; Zhu, X. F. Analysis on chemical and physical properties of bio-oil pyrolyzed from rice husk. J. Anal. Appl. Pyrolysis. 2008, 82, 191–198.
(31) Shen, J.; Wang, M.; Wu, Y.; Li, F. Preparation of mesoporous carbon nanofibers from the electrospun poly(furfuryl alcohol)/poly(vinyl acetate)/silica composites. RSC. Adv. 2014, 4, 21089.
(32) Pan, Y.; Yu, J.; Wang, C.; Zhang, L.; Xu, N. Versatile preparation of monodispersive poly(furfuryl alcohol) and carbon hollow spheres in a simple microfluidic device. Chem. Commun. 2010, 46, 3732–3734.
(33) Hu, B.; Wang, K.; Wu, L.; Yu, S.-H.; Antonietti, M.; Titirici, M.-M. Engineering Carbon Materials from the Hydrothermal Carbonization Process of Biomass. Adv. Mater. 2010, 22, 813–828.
(34) Xiao, N.; Wei, Y.; Li, H.; Wang, Y.; Bai, J.; Qiu, J. Boosting the sodium storage performance of coal-based carbon materials through structure modification by solvent extraction. Carbon. 2020, 162, 431–437.
(35) Jiang, T.; Budarin, V. L.; Shuttleworth, P. S.; Ellis, G.; Parlett, C. M. A.; Wilson, K.; Macquarrie, D. J.; Hunt, A. J. Green preparation of tuneable carbon–silica composite materials from wastes. J. Mater. Chem. A. 2015, 3, 14148–14156.
(36) Song, L.; Feng, D.; Campbell, C. G.; Gu, D.; Forster, A. M.; Yager, K. G.; Fredin, N.; Lee, H.-J.; Jones, R. L.; Zhao, D.; Vogt, B. D. Robust conductive mesoporous carbon–silica composite films with highly ordered and oriented orthorhombic structures from triblock-copolymer template co-assembly. J. Mater. Chem. 2010, 20, 1691.
(37) Usami, Y.; Hongo, T.; Yamazaki, A. Thermal stability and behavior of platelet-shaped SBA-15 containing Zr. J. Porous Mater. 2011, 19, 897–902.
(38) Singh, A. S.; Patil, U. B.; Nagarkar, J. M. Palladium supported on zinc ferrite: A highly active, magnetically separable catalyst for ligand free Suzuki and Heck coupling. Catal. Commun. 2013, 35, 11–16.
(39) Ghasesmi, S.; Karim, S. Mizoroki–Heck Cross-Coupling Reaction of Haloarenes Mediated by a Well-Controlled Modified Polyacrylamide Brush Grafted Silica/Pd Nanoparticle System. Bull. Chem. Soc. Jpn. 2017, 90, 485–490.
(40) Parker, H. L.; Sherwood, J.; Hunt, A. J.; Clark, J. H. Cyclic Carbonates as Green Alternative Solvents for the Heck Reaction. ACS. Sustain. Chem. Eng. 2014, 2, 1739–1742.
(41) Jiménez González, C.; Curzons, A.; Constable, D. C.; Cunningham, V. Cradle-to-gate life cycle inventory and assessment of pharmaceutical compounds. Int. J. Life. Cycle. Assess. 2004, 9, 114–121.
(42) Bucsi, I.; Matalin, Á.; Molnár, Á.; Juhász, K. L.; Kunfi, A. Heck coupling reactions catalysed by Pd particles generated in silica in the presence of an ionic liquid. Struct. Chem. 2017, 28, 501–509.
(43) Yu, J. H.; Shen, A.; Cao, Y. C.; Lu, G. Z. Preparation of Pd-Diimine@SBA-15 and Its Catalytic Performance for the Suzuki Coupling Reaction. Catalysts. 2016, 6, 17.
(44) Clark, J. H.; Macquarrie, D. J.; Mubofu, E. B. Preparation of a novel silica-supported palladium catalyst and its use in the Heck reaction. Green. Chem. 2000, 2, 53–56.
(45) Schaffner, B.; Holz, J.; Verevkin, S. P.; Borner, A. Organic carbonates as alternative solvents for palladium-catalyzed substitution reactions. Chem. Sust. Chem. 2008, 1, 249–253.
(46) Bayardon, J.; Holz, J.; Schäfler, B.; Andrushko, V.; Verevkin, S.; Preetz, A.; Börner, A. Propylene Carbonate as a Solvent for Asymmetric Hydrogenations. Angew. Chem., Int. Ed. 2007, 46, 5971–5974.
(47) Lenden, P.; Ylioja, P. M.; Gonzalez-Rodriguez, C.; Entwistle, D. A.; Willis, M. C. Replacing dichloroethane as a solvent for rhodium-catalysed intermolecular alkyne hydroacylation reactions: the utility of propylene carbonate. Green. Chem. 2011, 13, 1980–1982.
(48) Schmidt, A. F.; Smirnov, V. V.; Al-Halaiga, A. Kinetics of the Heck reactions of styrene with bromobenzene and iodobenzene in the presence of ligandless catalytic systems: A comparative study. Kinet. Catal. 2007, 48, 390–397.
(49) Heck, R. F.; Nolley, J. P. Palladium-catalyzed vinylic hydrogen substitution reactions with aryl, benzyl, and styryl halides. J. Org. Chem. 1972, 37, 2320–2322.
(50) Jiang, T. Development of novel mesoporous silica and carbon materials. University of York, 2015.
(51) Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B. F.; Stucky, G. D. Nonionic Triblock and Star Diblock Copolymer and Oligomeric Surfactant Syntheses of Highly Ordered, Hydrothermally Stable, Mesoporous Silica Structures. J. Am. Chem. Soc. 1998, 120, 6024–6036.