Article

Catalytic Activity of Incorporated Palladium Nanoparticles on Recycled Carbon Black from Scrap Tires

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ABSTRACT: A stable support substrate for catalytically active metal nanoparticles (NPs) plays an important role in various chemical transformation reactions. This study describes the effective integration of catalytically active palladium nanoparticles (PdNPs) into recycled carbon black (rCB) obtained from scrap tires. The loading efficiency and dispersion degree of PdNPs prepared via a deposition−precipitation method are thoroughly compared to those prepared with conventional Vulcan CB. As the rCB powder exhibits relatively larger surface areas and wider pore size distributions, slightly polydisperse and more PdNPs are integrated across rCB than those on CB. These composite materials are subsequently tested as catalysts in the Suzuki coupling and styrene hydrogenation reactions. For the Suzuki reaction using phenylboronic acid and bromobenzene, the PdNPs on rCB exhibit slightly higher reactivity than those on CB (TOF of ∼9/h vs ∼8/h), presumably due to the structural features of the integrated PdNPs and the relatively hydrophobic characteristics of the rCB substrate. For the hydrogenation reaction, both composite materials easily result in over 99% yield under ambient conditions with similar activation energies of ∼32 kcal/mol. These composite materials are also recyclable in both reactions without a detectable loss of the PdNP catalyst and its activity. Understanding the physicochemical properties of rCB and demonstrating their potential use as a catalyst support substrate evidently suggest the possibility of replacing conventional CB, which also provides an idea of upcycling waste tires in the development of practical and green reaction systems.
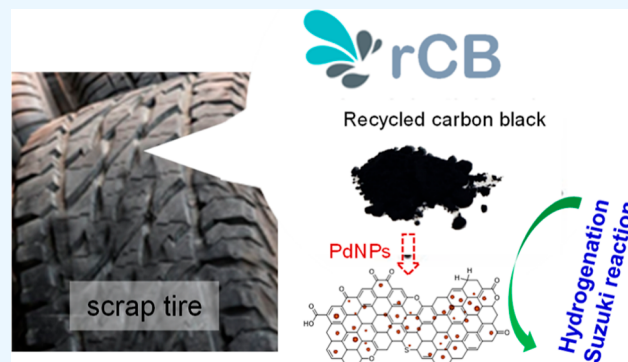
INTRODUCTION

Generating massive amounts of waste tires from the transportation industry has caused considerable environmental concerns, as around 75% of them have been deposited in landfills without any treatment.[1] Among many recycling methods, anaerobic pyrolysis of scrap tires at high temperatures has been a promising process to produce carbon black (CB) materials,[2−4] which are further pulverized to prepare recycled carbon black (rCB) in powder form. The relatively inexpensive production cost of rCB with a significantly less polluted recycling process could make it an alternative carbonaceous material. The handling of the resulting rCB is as easy as conventional CB powder obtained from the incomplete combustion of petrochemicals.[5−7] However, the rCB powder has shown slightly inferior overall physicochemical properties and contains inevitable impurities originating from scrap tires.[8−11] These problematic issues often limit the practical use of rCB to completely replace conventional CB. As CB powder has been extensively consumed as an essential filler for tires, plastic materials, purification systems, and electronic components, numerous efforts have been devoted to improving the properties of rCB to fulfill the requirements of

CB-based fillers.[8,9,12,13] Instead of regulating the physicochemical properties by utilizing extensive fabrication strategies, expanding their applicable usages as a current form without complicated modification could help the easy and practical consumption of rCB in various fields.

In this study, rCB powder is employed as a support substrate for catalytically active metal nanoparticles (NPs) without any pretreatment. When designing catalytic systems, the use of host substrates could readily enhance the stability of guest metal NPs, which can often display synergistic effects in many chemical reactions.[14−17] Thus, the surface areas and pore size distribution of rCB obtained from scrap tires were initially examined to compare the uptake capability to conventional Vulcan CB. Subsequently, a deposition−precipitation (D−P) method was utilized to integrate palladium (Pd) ions, which
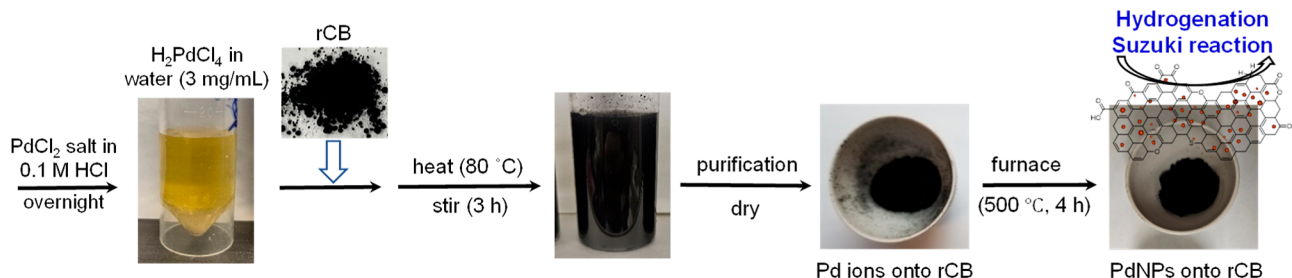
Figure 1. Formation of PdNP-loaded rCB (or CB) composite materials as catalysts.

were then thermally transformed into palladium nanoparticles (PdNPs) at a high temperature.[14,18,19] The integrated PdNPs were then tested as catalysts in the Suzuki coupling reaction and hydrogenation of styrene in ethanol-rich aqueous solvents.[18,20−25] Comparing the loading efficiency of PdNPs onto CB and rCB and their catalytic properties in these two model reactions could allow for an understanding of the intrinsic contributions and/or roles of catalyst support substrates. It revealed that the overall catalytic functions of the PdNP−rCB were as good as (or slightly better than) the PdNP−CB composite materials in these two reactions under green conditions. These results strongly suggest that the rCB can serve as an alternative support substrate to possibly replace conventional CB. Therefore, this study provides the evident idea of utilizing the rCB powder recycled from troublesome waste tires in the area of novel catalyst designs. Furthermore, the diverse catalytic functions of rCB-based composite materials capable of operating in green solvent environments can be an additional bonus feature when developing catalytic systems. The strategy developed in this work can be easily reproduced to incorporate other metal NPs on rCB that can serve as cost-efficient, reactive, and green catalysts for various chemical reactions.

EXPERIMENTAL SECTION

Integration of PdNPs onto CB and rCB Via Deposition−Precipitation (D−P). The integration of PdNPs onto CB and rCB was accomplished by a slight modification of the D−P method.[19,26,27] Water-soluble Pd salts, H_2PdCl_4, were initially prepared by suspending 1.0 g of $PdCl_2$ in 100 mL of 100 mM HCl overnight. The resulting dark-brown solution (10 mg/mL) was diluted with pure water to reach a final Pd salt concentration of 3.0 mg/mL. An aliquot of this H_2PdCl_4 solution (80 mL) in an Erlenmeyer flask was adjusted to a pH of ~9.5 by slowly adding ~9.6 mL of 1.0 M KOH. After introducing 0.8 g of CB (or rCB), this final mixture was sonicated and placed in an oil bath, which was then heated to 80 °C for 3 h. The reaction mixture was centrifuged at 10,000 rpm for 30 min three times to remove any free Pd ions. The final precipitates were dried in an oven at 50 °C overnight, resulting in a brownish-black powder. The dried powder was thermally reduced in a muffle furnace at 500 °C for 4 h in air. The integrated PdNPs onto the CB (or rCB) were then used as catalysts.

Suzuki−Miyaura Coupling Reaction Using the PdNP-Loaded CB (or rCB). The Suzuki coupling between aryl boronic acid and aryl halide was employed as an initial model reaction to examine the catalytic property of CB (or rCB) integrated with PdNPs. Phenylboronic acid (PBA, 0.032 g; 0.26 mmol), bromobenzene (0.027 mL; 0.26 mmol), K_2CO_3 (0.10 g; 0.72 mmol), and a mixed solution of EtOH and water

(2.7 and 0.3 mL) were added to a 20 mL round-bottom vial. Fifteen milligrams of the composite materials (~0.6 mg of Pd content by AA analysis) were introduced to the reaction mixture, which was briefly sonicated and heated to 80 °C. After 6 h, the reaction mixture was cooled to room temperature, where the top solution (~1 mL) was transferred to Eppendorf tubes and separated by centrifugation at 10,000 rpm for 5 min for gas chromatography (GC) analysis. The percent conversion was estimated by examining the peak areas of the biphenyl standard solutions. The precipitated composite materials were recovered after the purification with a mixture of EtOH and water (9:1 ratio) for the recycling test. For the kinetic studies, the reaction was scaled up to 6.0 mL, and an aliquot (~0.5 mL) was taken at fixed time intervals for the GC analysis. In the case of chlorobenzene, the same reaction was also carried out in DMF at 120 °C for 6 h.

Hydrogenation of Styrene Using the PdNP-Loaded CB (or rCB). The composite materials were also tested as catalysts in the hydrogenation of styrene.[24,25,28] A small amount of PdNP−CB (or PdNP−rCB) composite materials (10 mg) were fully suspended in 10 mL of EtOH in a 50 mL beaker containing a stir bar. An aliquot (6.0 mL) of styrene in EtOH (0.26 mM) and 4.0 mL of 30 mM $NaBH_4$ in water were subsequently added to the previous mixture. After vigorous stirring at ambient temperature (20 °C), the reaction mixture (~2 mL) was taken at fixed time intervals using a syringe and passed through a hydrophilic cellulose acetate membrane filter (25 mm with a 0.45 µM pore diameter, Thermo Scientific). The filtered solution was subjected to UV−vis analysis, which was compared to the corresponding standard curve using the Beer−Lambert law. The same reaction was also performed in an ice bath (0 °C) as a function of time to calculate the rate of reaction and activation energy (E_a) by using the Arrhenius equation. For the recycling test, the reaction was carried out in a 50 mL round-bottom centrifuge tube at the ambient temperature for 45 min, where the solution was subjected to UV−vis analysis, and the precipitates were purified with a mixture of EtOH and water (8:2 ratio). Separately, the standard solutions were prepared by a serial dilution method using the styrene stock solution (0.26 mM) to obtain a calibration curve. The solution used in this experiment was a pre-prepared mixture of EtOH and water (8:2 ratio), the same as the hydrogenation of styrene environments.

RESULTS AND DISCUSSION

Prior to the utilization of CB and rCB as support substrates for catalytically active metal NPs, the wettability of CB and rCB was examined by using a water droplet after preparing pellet-type samples (Figure S1). Although the dispersion of the conventional Vulcan CB and rCB powder was visually indistinguishable in water, the contact angle of water droplets

on the surface of the CB pellet appeared to be slightly lower than that on the rCB. This observation implies that the CB powder possesses slightly more hydrophilic functional groups (e.g., −OH, −COOH, etc.). The specific surface areas (S_{BET}) of CB and rCB were also estimated by the BET (Brunauer−Emmett−Teller) test (Figure S2). The calculated S_{BET} based on the N_2 gas adsorption−desorption isotherms was around 56.9 and 71.6 m^2/g for CB and rCB, respectively. Although the rCB powder possessed a slightly higher S_{BET} than the CB, both powder samples exhibited comparable isotherm curves with relatively small hysteresis loops, which suggested a similar N_2 gas adsorption capability. However, the rCB powder displayed a much wider distribution of pore sizes than CB (∼33.2 vs ∼2.6 nm). These CB and rCB powders were then employed as support substrates to integrate PdNPs by the D−P method (Figure 1). Initially, the $PdCl_2$ salt (dark brown) was suspended in 100 mM HCl overnight to form water-soluble H_2PdCl_4 (bright yellow). An aliquot of the yellow solution was diluted in water (3.0 mg/mL), and the pH was adjusted to ∼9.5 by slowly adding 1.0 M KOH. The resulting solution was mixed with CB (or rCB) and then heated to 80 °C for 3 h of impregnation. After the reaction, the Pd-ion-adsorbed CB powder was obtained by simple centrifugation and washing steps. The precipitated powder was initially dried in an oven (80 °C) and transferred to a crucible cup. Subsequently, the powder sample was placed in a furnace (500 °C for 4 h) to thermally reduce the adsorbed Pd ions to nanoscale Pd clusters, readily resulting in the formation of PdNPs on the CB (or rCB). This entire D−P process is an effective way to physically integrate PdNPs around the CB (or rCB) to form the final composite materials.

The structural characteristics of the CB and rCB were examined before and after the integration of PdNPs by field-emission scanning electron microscopy (FE-SEM) (Figure 2).
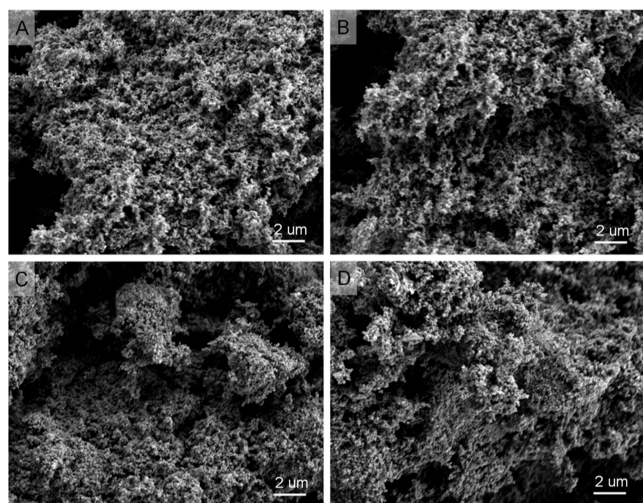

Figure 2. FE-SEM images of (A) CB, (B) rCB, (C) PdNP−CB, and (D) PdNP−rCB.

No significantly different structural features were observed between the Vulcan CB from the incomplete combustion of heavy petroleum products and the rCB from the waste tires via thermal pyrolysis.[2−4,8,29] Even after the integration of PdNPs, the FE-SEM images still showed similar morphological characteristics. However, their surfaces appeared slightly smooth, with somewhat decreased pore size/porosity (or

cavities) across the coagulated particles. These two comparable CB-based materials with rough surfaces were employed as stable support substrates to integrate catalytically active metal NPs.

Scanning transmission electron microscopy (STEM) images along with energy-dispersive X-ray spectroscopy (EDX) maps were obtained to confirm the successful integration and distribution of PdNPs across these CB-based substrates (Figures 3 and S3). The integrated PdNPs appeared to be relatively small but highly polydisperse on both CB substrates, which made it fairly difficult to precisely identify the size distribution. The surfaces of these randomly distributed PdNPs were expected to be free from any modifiers because the D−P method did not use any reducing or stabilizing agents. The STEM−EDX elemental maps confirmed the polydisperse PdNPs (green for Pd LX-ray) around CB (red for C KX-ray and yellow for O KX-ray) using the main atomic compositions. As the rCB powder with slightly hydrophobic characteristics had a higher tendency to undergo agglomerations in aqueous solution, the incorporated PdNPs also appeared to be a slightly agglomerated form of larger size. However, the dispersion degree of PdNP−CB and PdNP−rCB was comparable, which was monitored by turbidity (i.e., scattered light intensity) after suspending an equal amount of the composite powder in the EtOH-rich water solvent.

To examine the compositional information, X-ray photoelectron spectroscopy (XPS) analysis was carried out before and after the integration of the CB (or rCB) (Figure 4 and Table S1). From the survey scans, the conventional CB from petroleum hydrocarbons showed two distinctive peaks at ∼284 eV (C 1s) and ∼532 eV (O 1s), but the rCB displayed several additional peaks corresponding to Zn 2p (1020−1040 eV), Mn 2p (640−655 eV), S 2p (∼165 eV), and Si 2p (∼100 eV), which were also observed by others.[24,25] Unlike the CB spectrum, the presence of these detectable peaks suggested that the rCB from scrap tires contained a small amount of inevitable chemical elements originating from scrap tires. Upon the incorporation of PdNPs, both CB materials exhibited Pd core-level binding energy peaks $3d_{5/2}$ = 336.5 and $3d_{3/2}$ = 341.8 eV as a double with a splitting of 5.3 eV. In addition, the peak area ratio of $3d_{5/2}/3d_{3/2}$ = 4:3 is in good agreement with the typical Pd (0) element.[30−32] Thus, the XPS results clearly indicated that the D−P process readily allowed for the formation of PdNPs across both CB and rCB powder.

Powder X-ray diffraction (PXRD) was also employed to verify the formation and size variation of the integrated PdNPs onto the CB-based substrates (Figure 5). The CB from petrochemicals only showed two typical broad peaks at 2θ = 24.8 and 43.6° for the (002) and (101) planes, respectively, indicating amorphous carbon without any additives.[29] The rCB showed several additional sharp peaks for crystalline impurities, which often originated from rubber-based materials during pyrolysis.[33,34] Upon the integration of PdNPs, the characteristic Pd peaks at 40.1, 46.5, 68.1, and 82.2 corresponded to the (111), (200), (220), and (311) planes, respectively, which were comparable to those of typical crystalline PdNPs possessing the face-centered cubic structure (JCPDS card, file no. 46-1043).[32] Interestingly, several additional peaks appeared after the integration of PdNPs onto CB and rCB, which might have originated from the use of KOH during the D−P process. To support this speculation, a diffractogram of KOH powder was obtained and overlaid with those with PdNP−CB and PdNP−rCB (Figure S4). It was evident that
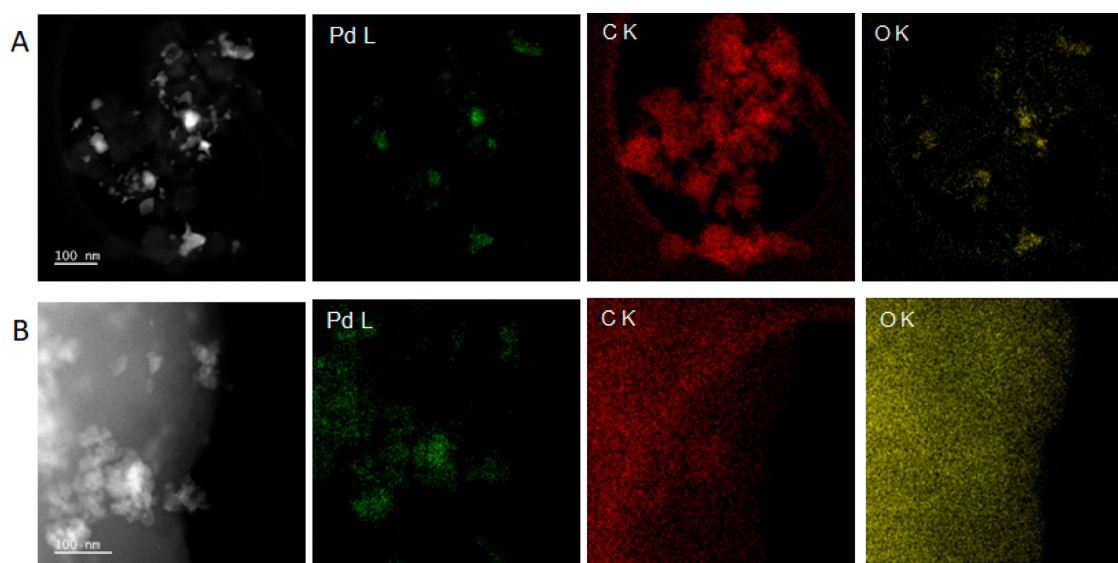
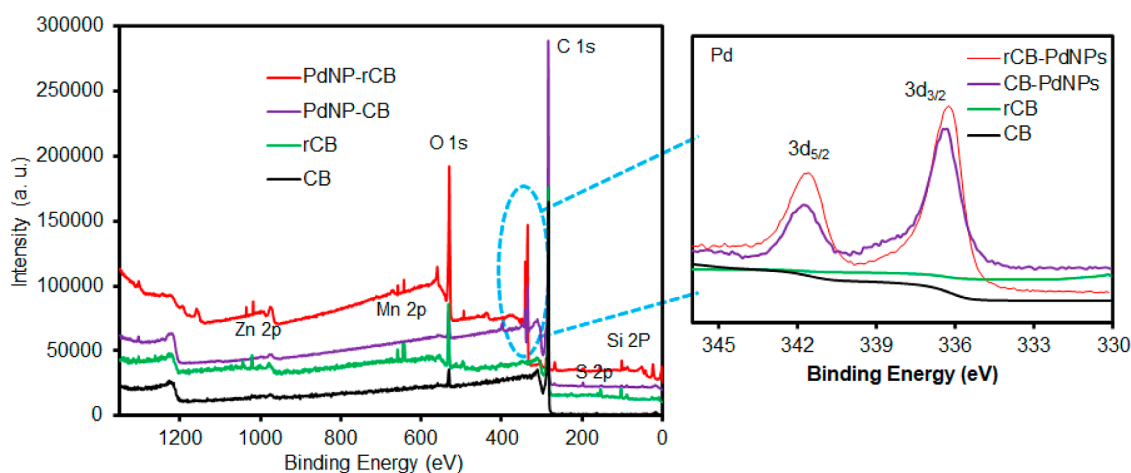**Figure 3.** STEM images and EDX maps of (A) PdNP−CB and (B) PdNP−rCB.

Figure 4. XPS spectra of CB, rCB, PdNP−CB, and PdNP−rCB.
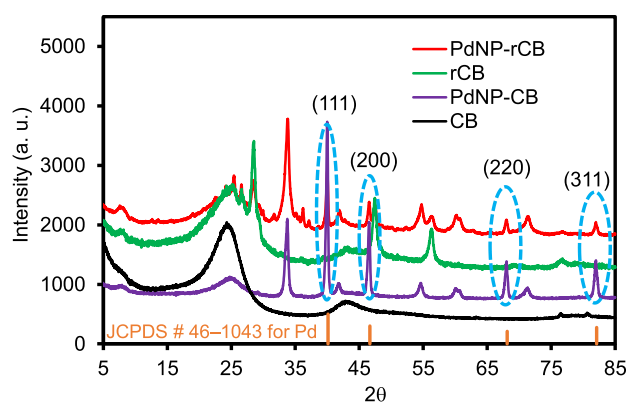

Figure 5. PXRD spectra of CB, rCB, PdNP−CB, and PdNP−rCB.

many of these peaks were well matched with KOH.[35,36] Separately, it has been reported that Pd^{2+}-doped metal oxides do not show any crystalline diffraction features from the ionic species.[37,38] Thus, the possibility that these additional peaks come from the residual Pd^{2+} ions can be eliminated.

To quantitatively examine the amount of integrated PdNPs on CB and rCB, atomic absorption spectroscopy analysis was performed after the composite particles were treated with nitric acid (Figure S5A). Based on the calibration curve obtained using a series of Pd standard solutions, the loaded amount of the integrated Pd atoms onto the CB and rCB was calculated. The D−P method allowed for CB and rCB to uptake the amount of Pd 12.7% (0.038 g) and 14.3% (0.043 g), respectively, based on the total amount of Pd salts used (0.3 g of $PdCl_2$ per 1 g of CB or rCB). It appeared that rCB uptook a slightly higher amount than CB, with presumably slightly larger surface areas examined by the S_{BET}. Thus, the integrated amount of Pd on carbonaceous substrates is calculated to be 0.038 mg per 1 mg of CB (3.8 wt %) and 0.043 mg per 1 mg of rCB (4.3 wt %), respectively. It is noted that the main goal of this initial study is to demonstrate the possibility of utilizing rCB obtained from scrap tires as a support substrate after thoroughly comparing their physicochemical property, uptake capability, and catalytic activity with CB. If rCB-based composite materials particularly exhibit as good as or better catalytic functions than conventional CB-derived composites under the same conditions, further regulation of physicochemical properties can potentially provide an idea of replacing commercial CB with sustainable and recyclable waste tires.

After examination of the structural and compositional properties of the integrated PdNPs onto CB (or rCB), their catalytic properties were then compared using the Suzuki cross-coupling reaction of PBA and iodobenzene under green solvent conditions (Figure 6). The coupling reaction with both
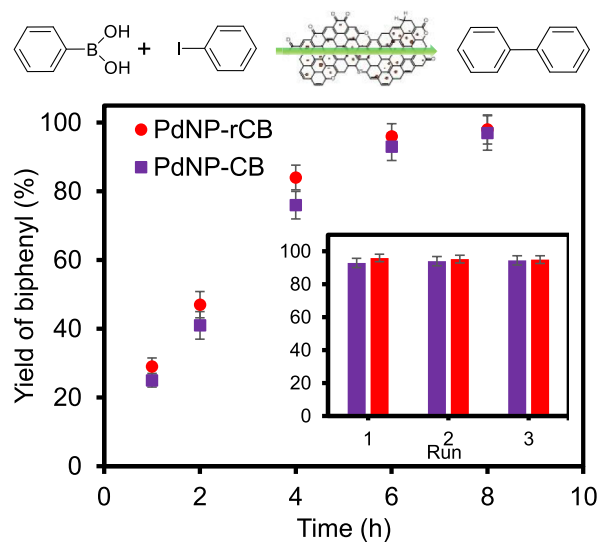

Figure 6. Suzuki coupling of PBA and iodobenzene in the presence of the composite materials as a function of time (inset graph presents the recyclability of the composite materials).

composite catalysts in pure EtOH resulted in the trace level formation of a biphenyl product ($<\sim$2%), which was probably caused by the limited solubility of the required inorganic base. Thus, the introduction of 10 vol % of water into the reaction mixture greatly improved the dissolution of K_2CO_3 base and ended up with high-yielding reactions under moderate temperatures and aerobic conditions. These two catalysts gradually increased the reaction yields as a function of time, where the PdNPs adsorbed onto rCB displayed slightly faster and higher yields than those on CB. As the incorporated PdNPs could be released from the CB support substrates and participated in the catalytic reaction,[39,40] the top solution of the mixture was dried and treated with HNO_3 for inductively coupled plasma optical emission spectroscopy after the reaction (Figure S5B). Based on the most reliable and sensitive calibration curve obtained from the emission line of 340.458 nm, the loss of Pd species was calculated to be nearly trace levels ($\sim$0.37 ppm from PdNP$-$CB and $\sim$0.45 ppm from PdNP$-$rCB). This negligible leaching may have a minimal impact on the main catalytic functions, as confirmed by the comparable reaction yields using recycled composite materials. It is noted that the extensive purification steps could result in a slight loss of the composite materials, but the overall reaction yields remained almost unchanged under our reaction conditions. To the best of our knowledge, this is the first incident to demonstrate the incorporation of PdNPs onto rCB substrates from scrap tires, and their catalytical activity and recyclability are as good as (even slightly better than) PdNPs on conventional CB. This EtOH-rich solvent system did not require additional extraction steps after the reaction due to the relatively good solubility of the biphenyl product, which offered great simplicity for evaluating the catalytic reactions.

To examine the intrinsic catalytic properties of the PdNP$-$CB and PdNP$-$rCB composite materials, a turnover frequency

(TOF) was calculated, which is a widely accepted method to compare the activity of catalysts.[21,41,42] Based on the yields of biphenyl after a 4 h reaction, the TOF values for both composite materials [i.e., TON (turnover number)/reaction time, where TON = molar quantity of the reactant/molar quantity of the catalyst] were $\sim$9/h for PdNP$-$rCB and $\sim$8/h for PdNP$-$CB, respectively, which are somewhat lower than other supported PdNP systems.[18,22,43] However, these comparable TOFs clearly indicated that the substrate functions of rCB are as good as those of the conventional CB for catalytic applications.

Given the comparable reactivity, the cross-coupling of additional reactants was carried out by using the composite materials under the same conditions (Table 1). The coupling

Table 1. Suzuki Coupling of PBA Derivatives and Arylbenzene[a]

Entry		Yield (%)	
		PdNP-CB	PdNP-rCB
(PBA, B(OH)₂)	(Cl-benzene)	~11 (~33)	~15 (~34)
(PBA, B(OH)₂)	(Br-benzene)	~74	~79
(PBA, B(OH)₂)	(I-benzene)	≥ 96	≥ 96
(4-methyl PBA, B(OH)₂)	(Br-benzene)	~73	~77
(4-methyl PBA, B(OH)₂)	(I-benzene)	≥ 97	≥ 97

[a]Reaction conditions: PdNP-loaded CB (or rCB) in a mixed solution of EtOH and water (9:1 ratio) at 80 °C for 6 h. The yields in the parentheses were obtained using the DMF solvent at 120 °C.

of PBA with arylbenzene evidently displayed the typical leaving group-dependent reactivity. Particularly, the reactivity of chlorobenzene possessing a relatively poor leaving group had detectably lower yields in the EtOH-rich solvent conditions. Slightly increasing the reaction temperature using the DMF solvent generally improved the overall conversion yields, possibly indicating that further optimization of reaction conditions could maximize the reaction yields. Separately, the coupling of 4-methyl PBA and arylboronic acid also resulted in similar trends. Generally, the reactivity of the integrated PdNPs onto rCB was comparable and slightly better than those onto CB, which supported the possibility of utilizing rCB as a support substrate for catalytic NPs in the chemical transformation reactions. It is noted that the carbon-based substrate in the D$-$P method increases the stability of integrated PdNPs without any capping agents, potentially enabling the presence of abundant surface areas (i.e., catalytic sites).

Furthermore, the composite materials were also tested in the hydrogenation of styrene, which was easily monitored with a UV$-$vis spectrophotometer (Figure 7A). Our initial attempt was to compare the catalytic activity of the PdNPs on CB and
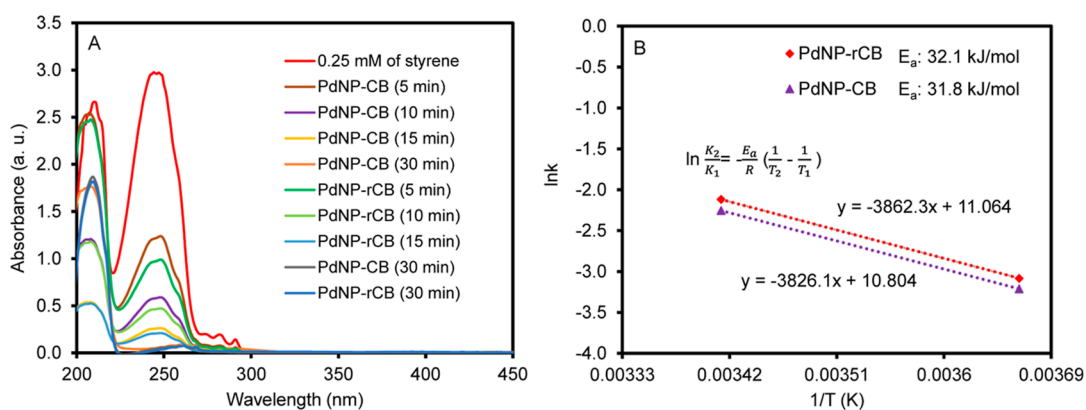
Figure 7. UV−vis spectra for (A) hydrogenation of styrene in the presence of PdNP−CB and PdNP−rCB as a function of time and (B) Arrhenius plots using the initial reaction rates at two different temperatures.

rCB in the EtOH-rich green reaction conditions. Interestingly, both composite materials rapidly converted styrene to ethylbenzene under our reaction conditions, which made it somewhat difficult to compare their reactivity. Thus, the reaction mixture was diluted enough to slow down the hydrogenation reaction. The conversion yields were calculated by using the standard curve of styrene (Figure S6). Based on the initial rate of reaction at the ambient temperature (20 °C), both composite materials were better suited to the first-order reaction, with $k = 0.105$/min for PdNP−CB and $k = 0.120$/min for PdNP−rCB, respectively. The same reactions were carried out in an ice bath (0 °C) as a function of time. Based on the initial reaction rates at these two different temperatures (Figure S7), the apparent activation energy (E_a) of both composite materials was calculated to be comparable (∼32 kJ/mol), which suggested similar temperature susceptibility (Figure 7B). This E_a value was somewhat higher for the catalytic hydrogenation of styrene than those reported in the literature.[44−46] However, the PdNPs loaded onto rCB still exhibited a slightly faster reaction rate than those loaded onto CB, given the loading efficiency and structural features. The yields of reactions with the recovered composite materials stayed nearly unchanged under the ambient temperature conditions, implying successful recyclability without any loss of catalyst properties (Figure S8A). Separately, the same reaction was carried out in the absence of the composite materials (i.e., catalysts), which did not show any meaningful absorbance changes of styrene even after 6 h, implying negligible hydrogenation only using a NaBH$_4$ hydrogen source without the catalysts (Figure S8B).

As the incorporated PdNPs onto the CB-based support substrate were formed in the absence of any stabilizing/capping agents, their catalytic functions could be further optimized with several reaction parameters, including reaction temperature, solvent, and the type of hydrogen sources, to fully utilize the readily available surfaces of PdNPs. The use of the rCB support substrate can offer many attractive aspects over conventional CB, including production cost, environmental concerns regarding a much less polluted production process and recyclability, and continuous sources of problematic tires. Demonstrating the applicability of scrap tires in rCB powder form and catalytically active metal NPs can provide an idea of upcycling environmentally concerning industrial rubber wastes. In addition, understanding the physicochemical and structural properties as well as the catalytic activities of the resulting composite materials under green solvent reaction conditions will lead to the development of safe and value-added chemical transformation reaction systems.

CONCLUSIONS

The fabrication of rCB obtained from scrap tires readily allowed for the preparation of green and inexpensive PdNP-integrated composite materials as reactive catalysts in these two chemical transformation reactions. Spectroscopic and microscopic characterizations evidently suggested the successful integration of PdNPs onto CB and rCB. The use of rCB as a support substrate possessing slightly larger surface areas and wider pore size distributions resulted in a relatively better loading efficiency of PdNPs with a higher polydispersity. Thus, the PdNPs on rCB displayed enhanced catalytic activities in the Suzuki cross-coupling reaction and hydrogenation of styrene compared to those on conventional CB. Both composite materials were also recyclable multiple times in these two reactions without any noticeable loss of the PdNP catalyst. Furthermore, both reaction environments established in this study, including EtOH-rich aqueous solvents and ambient conditions, offer the simplicity and practicability of the reaction setup. The introduction and further fabrication of catalytically active metal NPs could help to design reactive and sustainable catalysts under green conditions. Overall, demonstrating the effective utilization of rCB as a catalyst support substrate can provide an upcycling idea of a globally concerning waste resource that can even possibly replace conventional CB without any modification.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.4c05382.

> Additional experimental information and results are provided to clarify the formation of the composite particles and their physicochemical properties for catalytic applications (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ABBREVIATIONS

CB, carbon black; rCB, recycled carbon black; PdNPs, palladium nanoparticles; PBA, phenylboronic acid; TON, turnover number; TOF, turnover frequency

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