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A new synthesis of highly active Rh-Co alloy nanoparticles supported on N-doped porous carbon for catalytic C-Se cross-coupling and *p*-nitrophenol hydrogenation reactions

We reported new Rh-Co alloy nanoparticles supported on nitrogen-doped porous carbon through a simple ball milling method. The material exhibits high catalytic and recyclability activity in the C-Se coupling reaction and hydrogenation of *p*-nitrophenol. As featured in:



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A new synthesis of highly active Rh–Co alloy nanoparticles supported on N-doped porous carbon for catalytic C–Se cross-coupling and *p*-nitrophenol hydrogenation reactions[†]

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Bimetallic Rh–Co nanoparticles supported on nitrogen-doped porous carbon (Rh–Co/NPC) were synthesized from metal precursors and urea through a simple thermal decomposition/reduction under a nitrogen flow. The Rh–Co/NPC nanocatalyst which contains highly dispersed alloy nanoparticles (\sim 6 nm) showed high catalytic performance as well as good recyclability for the C–Se coupling reaction of diphenyl diselenide and aryl boronic acid and *p*-nitrophenol reduction.

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Introduction

Recently, bimetallic nanoparticles have been developed and have gained considerable attention because of their multiple unique properties compared to those of single metal nanoparticles, such as high electronic and optical properties, selectivity, and stability.¹⁻³ These improved properties were attributed to the combination of properties arising from two metals and the formation of new properties due to the synergistic effect of two metals.^{4,5} Owing to the advantageous properties, bimetallic nanoparticles have been used in many fields such as the biomedical and food industries and as catalysts.⁶⁻⁸ Many researchers have investigated the catalytic activity of bimetallic nanoparticles for many reactions. For example, Wisniewska and Ziolek reported a combination of Pt and Ag on a silica surface, which was applied for catalyzing the oxidation of methanol; this catalyst exhibited good activity with high conversion.⁶ In addition, the other metal combinations such as Ni and Pd have been reported to exhibit high electroactivity and serve as efficient catalysts for hydrogen production.⁹ Moreover, the Ni-Pd bimetallic nanoparticles have been reported as catalysts for C-C coupling reactions (e.g., Suzuki, Heck, and Sonogashira reactions), and the rate of conversion of reactants to products considerably increased using the Ni-Pd catalyst.¹⁰ Miyamura et al. also reported the high catalytic activity of the Rh–Pt bimetallic nanoparticles immobilized on polysilane for the hydrogenation of arene under mild conditions.¹¹ Thus, these reports demonstrate that a combination of two metals can increase the catalytic activity compared to catalysts comprising a single metal.

In addition to the above-mentioned metals, Rh and Co nanoparticles have been reported as transition-metal catalysts for organic reactions based on C-C and C-heteroatom bonds. Rhodium, as a single metal, is well known to have excellent catalytic activity toward many reactions, particularly electro-oxidation reactions, hydrogenation, and cross-coupling reactions.¹²⁻¹⁴ Similarly, cobalt also exhibits good catalytic activity toward cross-coupling reactions.¹⁵ However, because these metals easily aggregate and exhibit a decrease in their catalytic activity, they are considered as unstable catalysts and, thus, have limited applications. Some researchers reported that the use of carbon supports could resolve the problem of instability. Moreover, the construction of metalsupport interactions can improve the stability and durability of materials.¹⁶ Park et al. immobilized Co nanoparticles on charcoal to develop a catalyst for the Pauson-Khand reactions; this catalyst afforded a high product yield.17 Moreover, Rh deposited on fullerene-C60 was recently reported and applied for the catalytic reduction of 4-nitrophenol and Suzuki cross-coupling reactions.¹⁸ Based on previous reports, the combinative deposition of these two transition metals (Rh and Co) on carbon materials is expected to improve their catalytic activity.

Previously, Rh–Co bimetallic nanoparticles deposited on carbon materials have been developed for several reactions such as Pauson–Khand, hydroformylation, aminocarbonylation, reductive amination, and reductive cyclization.^{3,17,19–23} Also, few researchers have reported that Rh–Co bimetals are active for the C–Se coupling reaction.



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In the present work, we report new Rh–Co alloy nanoparticles supported on nitrogen-doped porous carbon (denoted as Rh–Co/NPC) through a simple one-pot reaction based on thermal treatment with a solid mixture of metal precursors and urea under a nitrogen gas flow (Scheme 1). The Rh–Co/NPC nanocatalyst was applied to a C–Se cross-coupling reaction for organoselenide production, which is very useful in the biochemistry field.^{24,25} Furthermore, the catalyst also showed high performance with good recyclability in catalytic *p*-nitrophenol hydrogenation. This result is supported by several reports which mention that the interaction between metals and supports (such as carbon materials) can enhance selectivity and yield in hydrogenation or reduction reactions.^{26–28}

Experimental

Chemicals

Rhodium(III) acetylacetonate (Rh(acac)₃, Rh(C₅H₇O₂)₃, 97%, Aldrich), cobalt(II) acetylacetonate (Co(acac)₂, Co(C₅H₇O₂)₂, 97%, Aldrich), and urea (CH₄N₂O, 99.0–100.5%, Aldrich) were used as received without further purification.

Synthesis of Rh-Co/NPC

For the synthesis of the Rh–Co/NPC nanocatalyst, 0.4 mmol of Rh(acac)₃ (0.16 g), 0.4 mmol of Co(acac)₂ (0.10 g) and 20.8 mmol of urea (1.25 g) were homogeneously mixed with methacrylate beads (diameter: 3/8 inch), using a high-energy ball mill (SPEX 8000M Mixer/Mill[®]) with 1725 rpm. After mixing for 5 min, the dark brown powder sample was transferred to an alumina boat in a tube furnace. The powder mixture was heated at a ramping rate of 5.6 °C min⁻¹ up to 700 °C under a flow of N₂ (200 mL min⁻¹) and thermally treated at the same temperature for an additional 120 min under continuous N₂ flow. After that, the resulting black powder was cooled to room temperature and collected. Different Rh/Co nanoparticle ratios (Rh₍₁₎–Co₍₃₎/NPC and Rh₍₃₎–Co₍₁₎/NPC) were synthesized and compared using the same method.

C-Se coupling reactions

Diphenyl diselenide (1 mmol), arylboronic acid (1.1 mmol), base (2 equiv.), and catalyst (3 mol%) were mixed in round bottom tubes. Then, 2 mL of solvent was added to the mixture using a syringe. The mixture was stirred at reflux under air for 24 h. After completion of the reaction, the mixture was cooled to room temperature, diluted with dichloromethane, and extracted with Na_2CO_3 solution several times. MgSO₄ was added to the extract, filtered, and evaporated using a rotary evaporator. The product was analyzed by using GC-MS.

Hydrogenation of *p*-nitrophenol

A total of 5 mmol of 4-NP in 1.5 mL aqueous solution was mixed with 40 mmol of fresh $NaBH_4$ in 10 mL of aqueous solvent and stirred using a magnetic bar. Then, 1 mg of catalyst was added to the mixture. Next, 0.8 mL of solution was taken from the mixture and diluted with distilled water and analyzed using UV-vis spectroscopy. This step was continued until a complete decrease in the 4-NP absorbance peak was observed.

Material characterization

TEM images and HAADF-STEM images were obtained using a Talos F200X operated at 200 kV. EDS and elemental analysis and mapping were performed using a higher-efficiency detection system (Super X: 4 windowless SDD EDS system). The XRD analysis was conducted on a high-power powder X-ray diffractometer (Rigaku D/MAX-2500, 18 kW). The N₂ sorption isotherms were measured at 77 K using a TriStar II 3020 surface area analyzer. Before measurement, the samples were degassed in vacuum at 573 K for 4 h. XPS was performed using a K-alpha (TM) system with a micro-focused monochromator X-ray source (Thermo VG Scientific, Inc.). Thermogravimetry (TG) measurement was measured using a SETARAM apparatus with a heating rate of 10 °C min⁻¹ under an air flow. The N content in the sample was measured by using an Oxygen-Nitrogen-Hydrogen analyzer (ONH-2000, ELTRA GmbH). Raman spectroscopy was performed using a microscope (Horiba Lab RAM HR Evolution Visible NIR) with a 514 nm laser. Gas chromatography-mass spectrometry (GC-MS) was performed on a Shimadzu GC-1010 Plus GCMS-QP2010 SE. UV-vis absorption spectroscopy was performed on the Shimadzu UV-1800 spectrometer.

Results and discussion

Synthesis of the Rh-Co/NPC nanocatalyst

Scheme 1 illustrates the synthesis of the Rh–Co/NPC nanocatalyst. First, Rh(acac)₃ and Co(acac)₂ as metal precursors and urea as an N-doped carbon support source were mixed in the solid state. Next, the thermal treatment of the solid mixture at 700 °C under an N₂ gas flow was conducted. At high temperatures, the Rh and Co precursors were decomposed and reduced to Rh–Co alloy nanoparticles. At the same time, urea was transformed to porous carbons with many defect sites which can partly organize small pores in the structure.

The transmission electron microscopy (TEM) image shows an overall structure of the Rh–Co/NPC nanocatalyst (Fig. 1a). The size of small nanoparticles dispersed on the porous carbon sheets was measured to be 6.2 ± 1.3 nm, counting 200 particles in the TEM images (Fig. 1b). The high-resolution TEM (HRTEM) image shows a spherical nanoparticle (Fig. 1c). The corresponding Fourier-transform (FT) pattern indicates that alloy formation of Rh–Co crystals with a distance of 0.21 nm between adjacent fringes well matched with the (111) plane of



Fig. 1 (a) TEM image, (b) size distribution histogram, (c) HRTEM image with the corresponding Fourier-transform pattern (inset of c), (d) HAADF-TEM image, (e and f) elemental (Rh and Co) mapping images, and (g) XRD spectrum of the Rh–Co/NPC nanocatalyst. The bars represent 40 nm (a), 4 nm (c), and 10 nm (d–f).

RhCo alloy (inset of Fig. 1c). From the JCPDS data, the lattice distances for (111) planes are reported as 0.2119 nm at CoRh alloy (JCPDS No. 01-071-7421), 0.2047 nm at Co (JCPDS No. 15-0806), and 0.2196 nm at Rh (JCPDS No. 05-0685), respectively. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image clearly shows alloy metal regions as bright dots and carbon support regions as muddy clouds (Fig. 1d and Fig. S1 in the ESI†). The elemental mapping of Rh (green) and Co (red) also demonstrates the formation of well-dispersed alloy nanoparticles supported on

carbon (Fig. 1e and f). The X-ray diffraction (XRD) spectrum of the Rh–Co/NPC nanocatalyst shows representative peaks at $2\theta = 33$ and 36° , which are assigned to the reflections of (111) and (200) planes in the face-centered-cubic (fcc) phase CoRh (Fig. 1g). Using the Debye–Scherrer equation, the average size of Rh–Co alloy is estimated to be 6.3 nm from the broadness of the (111) peak; this value is well-matched with the particle size determined from the TEM images.

From the energy-dispersive X-ray spectroscopy (EDS) data, the atomic ratio of Rh and Co was measured to be 1.0 (Rh: 49.8% and Co: 50.2%) (Fig. S2 in the ESI†). In the Rh– Co/NPC nanocatalyst, the content of carbon support was estimated to be 36.2 wt% by thermogravimetric analysis (TGA) (Fig. S3 in the ESI†).

The N₂ sorption experiments for the Rh–Co/NPC nanocatalyst exhibited a type IV adsorption–desorption hysteresis (Fig. 2a). The Brunauer–Emmett–Teller (BET) surface area and the total pore volume were calculated to be 385 m² g⁻¹ and 0.26 cm³ g⁻¹, respectively. Applying the Barrett–Joyner–Halenda (BJH) method, the small pore size was found to be 4.1 nm by the desorption branch (Fig. 2b).

The X-ray photoelectron spectroscopy (XPS) spectrum was measured to confirm the surface states of the Rh–Co/NPC nanocatalyst. The dominant signals in the XPS spectrum were originated from Co, O, N, C, and Rh (Fig. 3a). The XPS spectrum of the energy region of the Rh bands shows one set of peaks (at 307.1 and 311.9 eV) in the range of the Rh 3d_{5/2} and 3d_{3/2} orbital signals, corresponding to the Rh⁰ state (Fig. 3b). The N 1s spectrum of the Rh–Co/NPC nanocatalyst revealed two split peaks at 398.2 and 400.8 eV corresponding to pyridinic N and pyrrolic N (Fig. 3c). The total N content in the Rh–Co/NPC



Fig. 2 (a) N_2 adsorption/desorption isotherms and (b) pore size distribution diagram of the Rh–Co/NPC nanocatalyst.



Fig. 3 (a) XPS survey spectra of the Rh–Co/NPC nanocatalyst and XPS spectra in the energy regions of (b) Rh 3d and (c) N 1s. (d) Raman spectra of the Rh–Co/NPC nanocatalyst.

sample was found to be 4.2 wt% by using a nitrogen analyzer (OHN-2000).

In the Rh–Co/NPC nanocatalyst, the carbon crystallinity and disorder in sp² hybridized carbon were monitored by using Raman spectroscopy (Fig. 3d). The Raman spectrum shows a strong peak around 1357 cm⁻¹ (D-band) that was caused by the disordered structure and defect sites associated with dangling bonds for the in-plane termination of carbon atoms. The G band at ~1584 cm⁻¹ corresponds to the E_{2g} phonon of the bonded carbon atoms in a 2D hexagonal lattice. In the spectrum, the high I_D/I_G value (1.1) was observed, indicating the presence of many disordered sites such as small sp² domains and defective carbon pores.

Catalytic performance of Rh-Co/NPC

The catalytic activity of Rh-Co/NPC for C-Se cross-coupling reactions using diphenyl diselenide and phenyl boronic acid as substrates was evaluated to optimize the reaction conditions. Initially, diphenyl diselenide and phenyl boronic acid reactions in DMSO at 110 °C for 24 h were completed in the presence of various bases. Compared to other bases, the presence of K₂CO₃ afforded the highest product yield (78%; Table 1, entry 5). In addition, in the presence of KOH as the base, a moderate yield of 61% was obtained (Table 1, entry 1). However, NaOH, Na₂CO₃, and Cs₂CO₃ did not give good results (33, 28, and 41% yields, respectively) because of the low substrate-product conversion rate. Based on this result, K₂CO₃ was selected as the optimal base. Next, we proceeded to screen the optimal solvent for this reaction. Several solvents including protic and aprotic were used. No product was afforded when water or THF was used as the solvent (Table 1, entries 7 and 9, respectively). The DMSO:H₂O mixture and DMF afforded low yields (37% and 57%; Table 1, entries 6 and 8, respectively). Therefore, DMSO was selected as the optimal reaction solvent.

NPC nanocatalyst										
B(OH) ₂										
Se Se + Column Action Se Se Se + Column Action Se										
Entry	Amount catalyst	Solvent	Base	Time (h)	Yield ^a (%)					
1	1 mol%	DMSO	КОН	24	61					
2	1 mol%	DMSO	NaOH	24	33					
3	1 mol%	DMSO	Na_2CO_3	24	28					
4	1 mol%	DMSO	Cs_2CO_3	24	41					
5	1 mol%	DMSO	K_2CO_3	24	78					
6	1 mol%	$DMSO: H_2O$ (1:1)	K_2CO_3	24	37					
7	1 mol%	Water	K_2CO_3	24	Trace					
8	1 mol%	DMF	K_2CO_3	24	57					
9	1 mol%	THF	K_2CO_3	24	Trace					
10	2 mol%	DMSO	K_2CO_3	24	87					
11	3 mol%	DMSO	K_2CO_3	24	92					
12	3 mol%	DMSO	K_2CO_3	18	66					
13	3 mol%	DMSO	K_2CO_3	36	83					
14	3 mol% Co(acac) ₂	DMSO	K_2CO_3	24	Trace					
15	3 mol% Rh(acac) ₃	DMSO	K_2CO_3	24	Trace					
16	3 mol% urea	DMSO	K_2CO_3	24	Trace					
17	3 mol% Rh/ NPC	DMSO	K_2CO_3	24	49					
18	3 mol% Co/ NPC	DMSO	K_2CO_3	24	36					
19	3 mol% (14 + 15 + 16)	DMSO	K ₂ CO ₃	24	Trace					
20	3 mol%	DMSO	K_2CO_3	24	62					

Reaction conditions: diphenyl diselenide (1 mmol), phenyl boronic acid (1.1 mmol), base (2 equiv.), and solvent (2 mL). ^{*a*} Yields determined by using GC-MS.

(17 + 18)

Furthermore, we screened the optimal catalyst amount. When the amount was increased from 1 mol% to 2 mol% and 3 mol%, the yield significantly increased to 87% (2 mol% catalyst) and 92% (3 mol% catalyst) (Table 1, entries 10 and 11, respectively). This shows that the catalyst amount influences the conversion of reactants to the product. Furthermore, the reaction was conducted over different reaction times. The yield decreased to 66% when the reaction was conducted for 18 h (Table 1, entry 12). Interestingly, when the reaction was conducted for 36 h, the yield decreased to 83% (Table 1, entry 13). Thus, for further experiments, we used the following optimized conditions: 3 mol% as the catalyst amount, K_2CO_3 as the base, DMSO as the solvent, 110 °C as the reaction temperature, and 24 h as the reaction time. For comparison, we examined other catalysts (3 mol% Co(acac)2, Rh(acac)3, and urea as raw materials for the synthesis of Rh-Co/NPC) for the C-Se cross-coupling reactions under the optimized conditions. However, no product was formed when these compounds were individually used as the catalyst (Table 1, entries 14-16). The same result also occurred when a mixture of these three compounds was used as the catalyst (Table 1, entry 19). In addition, low conversion rates were achieved when only Rh (particle size: 4.7 nm) and Co

(particle size: 6.7 nm) nanoparticles were used as catalysts (49% and 36%; Table 1, entries 17 and 18, respectively). The yield increased moderately (62%) when a mixture of Rh and Co nanoparticles was used (Table 1, entry 20). Moreover, different Rh/Co nanoparticle ratios ($Rh_{(1)}$ – $Co_{(3)}$ /NPC and $Rh_{(3)}$ – $Co_{(1)}$ /NPC) show lower yield compared to Rh–Co/NPC with 72 and 79% yields, respectively (Table 3). This shows that the ratio of metal nanoparticles has an effect on the catalysis process to influence the conversion.

Furthermore, we checked the C-Se cross-coupling reactions using various phenylboronic acids with diphenyl diselenide under the optimized conditions. Generally, the target products were produced in good to excellent yields. Electron-donating groups, such as *p*-OCH₃, which attach to phenylboronic acid, afforded a high yield of 91% (Table 2, entry 2). In addition, the two methoxy groups at the ortho position showed a high conversion rate and afforded 92% yield (Table 2, entry 3). Electron-withdrawing groups such as p-CF₃, p-CO₂Et, o-CHO, and *p*-F afforded a high yield of approximately 92%, 88%, 94%, and 93%, respectively (Table 2, entries 4-7). Various heteroatomic boronic acids were used to react with diphenyl diselenide, resulting in good yields (Table 2, entries 8 and 9). These results showed that this catalyst under the optimized conditions could be used with various reactants. In addition, the comparison of the C-Se cross-coupling reactions with other catalysts was displayed in Table 3 which shows that Rh-Co/NPC has good catalytic activity.

The catalytic activity of Rh-Co/NPC was also investigated for the hydrogenation of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) using NaBH₄ as the reducing agent. Initially, 4-NP in an aqueous medium exhibited UV-vis absorption at 317 nm. However, this absorption peak shifted to approximately 400 nm when NaBH₄ was added to the solution. This changed the color from light yellow to bright yellow. This shows the formation of 4-nitrophenol ions (4-NPI) in the solution (Fig. 4a). The maximum absorption peak of 4-NPI remained unchanged when Rh-Co/NPC was not used for the reaction, which indicated that the hydrogenation of 4-NP to 4-AP did not occur. A new absorption peak was observed at around 300 nm that can be ascribed to the formation of 4-AP, followed by a decrease in the absorption peak of 4-NP when a small amount of the catalyst was used (Fig. 4b). In addition, the solution became colorless. In this reaction, different conditions such as 4-NP concentration, NaBH₄ concentration, and catalyst amount were investigated at room temperature. The $\ln(C/C_0)$ versus time plot in Fig. S5 (ESI[†]) was determined from the absorbance peak, and the slopes were used to obtain rate constant k.

First, the catalyst amount was studied for 4-NP hydrogenation using 5 mmol of 4-NP and 40 mmol of NaBH₄. Fig. S6 (ESI[†]) shows the UV-vis absorption spectra of 4-NP in the presence of various catalyst amounts. The spectra showed that as the catalyst amount increased, the 4-NP hydrogenation rate also increased. When 0.5 mg of catalyst was used, a complete hydrogenation of 4-NP occurred after 14 min. Increasing the catalyst amount to 1 and 1.5 mg decreased the reaction time to 6 and 5 min, respectively, and increased the k value Fig. 4c.

 Table 2
 Reactant scope C-Se coupling reactions using the Rh-Co/NPC nanocatalyst



Therefore, 1 mg of catalyst was used for further investigation because there was no noticeable reaction time difference when 1 and 1.5 mg catalysts were used.

The effect of the 4-NP concentration was also explored, while the other conditions were constant (1 mg of catalyst and 40 mmol of NaBH₄). Fig. 4d shows a decrease in the rate constant with increasing 4-NP concentration. Increasing the 4-NP concentration from 3 to 7 mmol induced the conversion of 4-NP to 4-AP (Fig. S7, ESI[†]). This could happen because the catalyst can absorb 4-NP and compete with BH_4^- , thereby decreasing the number of sites on the catalyst surface; this facilitated the interaction between the catalyst and BH_4^- and

Table 3 The comparison of the C–Se cross-coupling reactions with other catalysts

Catalyst	Amount of catalyst (mol%)	Reaction time (min)	Yield (%)	Ref.
Fe, FeCl ₂ or FeCl ₃	10	20	91	29
Nano CoFe ₂ O ₄	5	8	14	30
Cu ₂ O-bpy, Mg	5	30	94	31
CuI-bpy	5	12	93	32
$Rh_{(1)}$ - $Co_{(3)}/NPC$	3	24	72	This work
$Rh_{(3)}$ -Co ₍₁₎ /NPC	3	24	79	This work
Rh-Co/NPC	3	24	92	This work



Fig. 4 (a) UV-vis spectra of hydrogenation of 4-NP and 4-NPI. (b) UV-vis spectra of hydrogenation of 4-NP using the Rh–Co/NPC nanocatalyst, (c–e) rate constant under different catalyst amounts, concentration of 4-NP, and concentration of NaBH₄.

promoted the transfer of H to 4-NP. Moreover, we investigated the effect of the NaBH₄ concentration, while the other conditions were constant (1 mg of catalyst and 5 mmol of 4-NP) (Fig. S8, ESI†). With the increase in NaBH₄ concentration, the rate constant also increased gradually (Fig. 4e). This is because at high NaBH₄ concentration, the amount of formed BH₄⁻ increases, which facilitates more electron transfer in this reaction. In contrast, low NaBH₄ concentration causes slow electron transfer to 4-NP. Based on these results, it can be concluded that catalyst amount, dye concentration, temperature, and NaBH₄ concentration affect the hydrogenation of *p*-nitrophenol due to the synergistic effect between all of these parameters.^{5,39} In

 Table 4
 The comparison of hydrogenation of *p*-nitrophenol reactions with other catalysts

Catalyst	Amount of catalyst	Dyes (mmol)	Reaction time (min)	Degradation rate (%)	Ref.
RGO-Pd ₁ (Co) ₁₅	0.12 mol%	1	5	99	33
Ag/ZnO flower like	150 mg	0.01	80	95	34
AgPd@UiO-66-NH ₂	1.5 mg	5	7	99	35
NaxWO ₃ /Ag ₂ O nanocomposite	1.5 mg	5	21	99	36
Fe ₃ O ₄ @COF-Au	3 mg	108	20	99	37
Rh-Co ₂ O ₃ /Al ₂ O ₃	100 mg	7.2	240	93	38
Rh-Co/NPC	1 mg	5	4	99	This work

addition, the comparison of hydrogenation of *p*-nitrophenol reaction with other catalysts was displayed in Table 4 which shows that Rh–Co/NPC has good catalytic activity with a short reaction time.

These two catalytic performance activities show that there are synergistic effects between Rh, Co, N, and C in C-Se coupling and *p*-nitrophenol hydrogenation reactions. The key factor that is affecting the success of a catalytic process is the electronic system interaction between metals and supporting materials.^{40–42} Moreover, the porous material and N dopant can also accelerate the catalytic process. This nitrogen dopant plays an important role in the synthesis process of small nanoparticles due to the coordination between the lone pair electron of N atoms and metal empty orbitals to form a strong interaction.43 In addition, the lone pair electrons of N dopants can conjugate with carbon materials by activating the delocalized π electron systems of a graphene framework. As a result of this electron conjugation, it can increase the active sites of the catalytic system and the electron transfer process. Furthermore, because the pyridinic N and pyrrolic N lone pair electrons cannot delocalize to the π electron systems of a graphene framework, they can coordinate with metal nanoparticle empty orbitals to increase the metal and support electronic interactions and the stability of the catalyst.^{40,41,44-46}



Fig. 5 The recyclability of Rh–Co/NPC for C–Se coupling reactions.

Paper

The recyclability of the Rh–Co/NPC nanocatalyst was explored for the C–Se coupling reaction using phenyl boronic acid and diphenyl diselenide under the optimized conditions. After the reaction, the nanocatalyst was separated and collected by centrifugation and reused for five cycles. Fig. 5 shows that the Rh–Co/NPC catalytic activity is still high without any significant decrease in yield. To verify the stability and durability of Rh–Co/NPC, the catalyst was recovered after the catalytic reaction and analyzed using TEM, as shown in Fig. S9 (ESI†). After the reaction, Rh–Co/NPC maintained its original structure and did not undergo severe particle aggregation.

Conclusions

The Rh–Co/NPC nanocatalyst (*ca.* 6 nm) was simply synthesized through a one-pot thermal decomposition method. The high catalytic activity was investigated for the C–Se coupling reaction with various arylboronic acid reactants. In addition, this nanocatalyst was active toward the hydrogenation of *p*-nitrophenol over a short reaction time (~ 6 min). The catalyst was used for 5 cycles of the C–Se coupling reaction without any noticeable decrease in product yields.

Conflicts of interest

There are no conflicts to declare.

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