






# Suzuki–Miyaura reaction and solventfree oxidation of benzyl alcohol by Pd/nitrogen-doped CNTs catalyst

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## ABSTRACT

Suzuki–Miyaura C–C coupling reactions were investigated with Pd/nitrogen-doped carbon nanotubes (Pd/N-CNTs) as a catalyst. Also, the same catalyst was examined for the solventfree oxidation of benzyl alcohol to benzaldehyde. Nitrogen-doped carbon nanotubes (N-CNTs) were synthesized from 1-ferrocenylmethyl(2-methylimidazole) and benzophenone via a chemical vapour deposition technique. Acetonitrile was used as a solvent and source of both carbon and nitrogen constituents of N-CNTs. Pd nanoparticles (Pd NPs) were successfully dispersed on N-CNTs via a metal organic chemical vapour deposition method. SEM, TEM, XRD, elemental analysis and ICP-OES measurements were used to characterize the nanomaterials. From the TEM analysis, it was observed that Pd NPs were spherical and with particle sizes ranging from 3 to 8 nm. For Suzuki C–C coupling reactions, phenylboronic acid, aryl halide, Pd/N-CNTs catalyst and a base (NaOAc, K<sub>2</sub>PO<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, NaOH, Et<sub>3</sub>N and Na<sub>2</sub>CO<sub>3</sub>) were used. The optimized experiments indicate that K<sub>2</sub>CO<sub>3</sub>, as the base, and ethanol/water (1:1 v/v, 10 mL) mixture, as a solvent, are the best reaction conditions. The solventfree oxidation reactions of benzyl alcohol were also done with Pd/N-CNTs catalyst and benzyl alcohol as a substrate. In both sets of reactions, C–C coupling and oxidation, the increase in pyrrolic nitrogen species was found to be responsible for higher catalytic activities of Pd/N-CNT catalysts, and this was attributed to the ease of Pd NP dispersion on N-CNTs, relative to pristine CNTs. Also, the higher catalytic activity of Pd/N-CNTs could be ascribed not only to the smaller Pd NP size or surface area, but to also the surface properties and the nature of the support when compared with the undoped counterpart, Pd/CNTs.

## Introduction

Efficient Suzuki coupling reaction of an aryl halide and boronic acids with less expensive substrates, and recyclable heterogeneous catalysts, is of economic

importance for pharmaceutical and fine chemical industries. The selective oxidation of benzyl alcohol with the use of molecular oxygen is one of the favourable routes for a greener synthesis of benzaldehyde [1], i.e. relative to metal oxidants such as

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permanganates and chromates. Benzaldehyde is an important intermediate in organic synthesis due to its application in the pharmaceutical [2], cosmetic [3] and food packaging [4] industries, among other useful applications. On the other hand, palladium (Pd) metal has been intensively used as a catalyst in a wide range of catalytic processes, such as oxidation [5], hydrogenation [6, 7] and C–C coupling reactions [8, 9]. Pd metal catalyst has been found to be very useful, especially in homogeneous catalysis as it is relatively more selective, however, the use of homogenous Pd metal catalyst remains a challenge and uneconomical for large-scale preparation. Hence, heterogeneous catalysis is sometimes preferred. Under heterogeneous catalysis, Pd nanoparticles (Pd NPs) have been supported on several substrates such as zeolites [10], polymers [11] and metal oxides [12, 13] for improved catalytic activity.

Due to poor interactions between catalyst active sites and reactants, coupled with the unavailability of active site on some aforementioned supports, shaped carbon nanomaterials (SCNMs), such as carbon nanotubes (CNTs), carbon sphere (CS), carbon fibres (CF) and graphene, are among the most sought-after alternative supports. In the case of CNTs, they are known to enhance the deposition of active metal crystallites and regulate substrates access on supported metal nanoparticles [14]. Reports also show that CNTs demonstrate superior catalytic activity due to their enhanced thermal stability and larger surface area, which is tuneable when employed as catalyst support [15–17].

CNTs have been synthesized via several methods: namely, arc discharge [18], laser ablation [19] and CVD techniques [20]. Among these methods, the CVD technique is widely employed for CNTs synthesis, and this is due to their relatively high deposition rates, easy scale-up and relatively easy removal of impurities from gaseous precursors [21]. CNTs have been employed as a support for metal nanoparticles for several catalytic applications due to their unique structural and electronic properties [22, 23]. The introduction of heteroatoms such as nitrogen into the graphitic matrix to give N-CNTs improves their potential catalytic applications, due to improved bulk and surface properties [24]. Similarly, CNTs surface modification via acid treatment introduces oxygen-functionalized groups (i.e. hydroxyl, carbonyl, lactones and quinone) on the N-CNTs surface which act as additional anchoring sites (apart

from the N-heteroatom) for Pd ions where the nucleation and growth of palladium nanoparticles (Pd NPs) are enhanced. Incorporation of these atoms (i.e. oxygen and nitrogen) introduces defects in CNTs [25]. These defects modify the dispersion, morphology, electronic structure, stability and surface area and ultimately enhance the catalytic performance of supported metal nanoparticles [26].

Pd nanoparticles as a catalyst have been widely employed for C–C coupling reactions; however, one of the setbacks in Pd heterogeneous catalysis is the Pd leaching aspect [27]. Heidenreich et al. [28] reported that Pd leaching could be prevented by fine-tuning of reaction conditions such as increasing reaction temperature and the introduction of reducing agents. However, this results in an increase in palladium particle size which leads to catalyst deactivation. Nevertheless, catalytic activities of CNTs as carbon support for Pd catalysts have been reported, especially for C–C coupling [29] and benzyl alcohol oxidation reactions [30]. However, there is not much work reported on the application of Pd/N-CNTs as supports for these reactions. Methods, such as electrodeposition [31] and metal–organic chemical vapour deposition (MOCVD) [32], have been employed for the deposition of Pd NPs on N-CNTs with latter approach still being the most efficient, cost-effective and environmentally friendly method [33].

There has been a lot of interest in Pd NPs supported on CNTs, and this is an ongoing research with continuous attempts towards modifying CNTs surface chemistry in order to improve the efficiency and greenness of the catalysts [34]. Interestingly, Pd NPs supported on N-CNTs have displayed promising catalytic activities in Heck coupling reactions [35], solventfree oxidation of benzaldehyde [36], Suzuki coupling [37] and hydrogenation reactions [38–40]. This has been associated with the type of nitrogen species incorporated [35, 41]. However, one of the major setbacks of Pd NPs anchored on N-CNTs is the uneven distribution of nanoparticles [42]. Hence, there is interest in achieving uniform dispersion of Pd NPs onto N-CNTs. To achieve better dispersion, oxygen functional groups such as carbonyl, carboxyl, lactone and quinone can be introduced in situ in the reactant mixture using water [43] or oxygen-containing aromatic compounds such as ethylbenzoate and benzaldehyde [44] to enhance N-CNTs wettability, thus leading to improved catalytic activity of N-CNTs. Also, the introduced surface oxygen

functionalities can enhance the dispersion of Pd NPs by acting as the anchoring sites [27]. Duan et al. [45] reported the fabrication of Pd NPs supported on mesoporous N-CNTs with ultrafine well-dispersed Pd NPs of 2–3 nm diameter size by the impregnation method. The improved catalytic performance of the Pd/N-CNTs catalyst was attributed to a strong interaction between Pd NPs and pyridinic-N atoms incorporated into the N-CNTs [45].

Herein, we report for the first time the use of 1-ferrocenylmethyl(2-methylimidazole) as a catalyst for the synthesis of N-CNTs. Also, the effect of oxygen on the surface properties of N-CNTs during synthesis has been investigated. In this study, the effect of oxygen-treated N-CNTs on Pd NPs properties such as particle size, stability and its dispersion on the catalytic activity and selectivity, compared to CNTs and N-CNTs counterpart, was explored. The effect of the type and distribution of N atom species, i.e. pyridinic-N, pyrrolic-N or quaternary-N atoms on Pd NPs dispersion and also the stability of the Pd/N-CNTs was also investigated. The catalytic activity of the resulting Pd/N-CNTs catalysts was compared to that of Pd/CNTs in Suzuki coupling and solventfree benzyl alcohol oxidation reactions. Some comparisons were made with a few examples in the literature. Also, the recyclability of the synthesized heterogeneous catalysts was examined.

## Experimental

### Materials

Ferrocenecarboxaldehyde (98%) and benzophenone (99%) were supplied by Sigma-Aldrich. Palladium(II) acetyl acetate ( $\text{Pd}(\text{acac})_2$ ) (99%), acetonitrile (99%), benzyl alcohol (98%), sodium borohydride (95%) and benzaldehyde (99%) were obtained from Merck Chemicals. All organic substrates were purchased from Sigma-Aldrich with 98–99% purity and were used as received without further treatment. Double-deionized water was used throughout the experiments.

### Synthesis of 1-ferrocenylmethyl(2-methylimidazole) catalyst

The general procedure described by Pan et al. [46] was followed in the synthesis of 1-ferrocenylmethyl(2-methylimidazole). Briefly, ferrocenemethanol

(1 mM) and 2-methyl-1H-imidazole (1.1 mM) mixture was refluxed in acetic acid for 6 h at 60 °C. The reaction was monitored on preparative TLC, with hexane/diethyl ether (v/v 2:1, 10 mL) as the eluent. Upon completion, it was neutralized and washed with 50% KOH in distilled water to remove excess acetic acid. The residue was chromatographed on a silica-packed column with  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (4:1) as the eluent. Yield: 68%; IR ( $\text{cm}^{-1}$ ) 703.82, 730.95, 896.20, 1264.38, 1422.24, 3055;  $^1\text{H-NMR}$  spectra ( $\text{CDCl}_3$ ) 2.27 (3H, s,  $\text{CH}_3$ ), 4.12 (9H, m, Cp), 4.73 (2H, s,  $\text{CH}_2$ ), 6.73 (1H, s, imidazole), 6.81 (1H, s, imidazole);  $^{13}\text{C-NMR}$  spectra ( $\text{CDCl}_3$ ): d (ppm) = 13.13, 23.75, 29.69, 45.84, 68.79, 77.30, 82.78, 118.99, 126.43, 128.799, 130.87, 143.94. LC-MS ( $\text{C}_{10}\text{H}_{16}\text{FeN}_2$ ) EI:  $[\text{M} + \text{H}^+]$   $m/z$  calc. 280.10022, found 281.10015.

### Preparation of CNTs, N-CNTs and N-CNT-1%

CNTs were synthesized by dissolving ferrocene (0.25 g) in toluene (9.75 g) to make 10 g precursor solution, while N-CNTs were synthesized by pyrolyzing 1-ferrocenylmethyl(2-methylimidazole) (0.25 g) in acetonitrile (9.75 g) at 850 °C (CVD method). In the case of N-CNT-1% synthesis, this was done by a mixing 1-ferrocenylmethyl(2-methylimidazole) (0.25 g) and benzophenone (0.5 g) (oxygen source) in acetonitrile (9.25 g). The symbol 1% represents the weight percentage of oxygen from benzophenone in the reactant mixture. The CVD procedure and set-up were followed according to the procedure described in previous reports [47]. In a typical experiment, the reactant mixtures were injected by a syringe at a rate of  $0.8 \text{ mL min}^{-1}$  through the quartz tube placed in a muffle furnace. The mixture was swept through the tube by 10% hydrogen in argon carrier gas, at a rate of  $100 \text{ mL min}^{-1}$ . After 30 min of reaction, the furnace was cooled to room temperature, and the product was collected from the reactor. Before use, the samples were calcined at 300 °C for 3 h to remove amorphous carbon and chemically treated by refluxing in 6M  $\text{HNO}_3$  under vigorous stirring at 120 °C for 24 h. Afterwards, the samples were washed with double-distilled water followed by ethanol and then dried at 100 °C. The resulting fluffy and black carbon materials obtained without and with benzophenone were labelled N-CNTs and N-CNTs-1%, respectively, and were characterized by

TEM, SEM, SAED, XRD, Raman, ICP-OES, DSC/TGA and XPS.

### Preparation of Pd/CNT, Pd/N-CNTs and Pd/N-CNTs-1% catalysts

The MOCVD technique, as outlined by previous reports [48], was employed for 0.02 mol% Pd loading onto CNTs and N-CNTs support. Pd(acac)<sub>2</sub> (0.048 g) was mixed with 0.316 g of acid-treated CNTs, N-CNTs and N-CNTs-1%, followed by thorough grinding, using a pestle and mortar. The resulting mixture was transferred into a stainless steel MOCVD reactor. The sealed MOCVD reactor was evacuated with the aid of a vacuum pump maintained at a partial pressure of  $2.1 \times 10^{-2}$  mbar for 40 min. The MOCVD reactor was then inserted into a CVD muffle furnace and heated at 120 °C for 30 min. The temperature was then ramped up to 300 °C at a rate of 2 °C min<sup>-1</sup> and thereafter maintained at 300 °C for 45 min. The obtained samples were kept under ambient condition and stored under an inert atmosphere for further applications.

### Characterization

X-ray diffraction patterns were recorded on a Rigaku/D<sub>max</sub> RB using a graphite monochromatized high-density Cu K $\alpha$  radiation ( $\lambda = 0.15406$  Å). Fourier transform infrared (FTIR) was recorded by the use of KBr pellets with PerkinElmer spectrum RX1 FTIR spectrometer. Raman spectra were recorded on DeltaNu Advantage 532<sup>TM</sup> Raman spectrometer with a 1 mW laser power on the sample compartment. Spectra were obtained with five accumulations at 1 min each. Microstructure images were obtained by scanning electron microscopy (SEM) (JOEL JEM 1010) and transmission electron microscopy (TEM) (JOEL JSM 6100). Higher magnifications were obtained from high-resolution transmission electron microscope (HRTEM) operated at 200 kV. N<sub>2</sub> adsorption-desorption isotherms and surface area of CNTs and N-CNTs were determined on a Micromeritics Tristar II surface area analyser. The Pd content of the catalysts was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) (PerkinElmer Optima 5300 DV). The thermal stabilities of CNTs and N-CNTs were measured using a Q Series<sup>TM</sup> thermal analyser DSC/TGA (Q600). The H<sub>2</sub>-TPR experiments were conducted in a gas mixture

containing 10% H<sub>2</sub> in Ar by Micromeritics Autochem II chemisorption analyser (2920) with the flow rate of 30 mL/min. X-ray photoelectron spectroscopy (XPS) analysis was carried out on a KRATOS AXIS Ultra DLD equipped with Al K $\alpha$  (1486 eV) X-rays, with X-ray power of 20 W and a beam diameter of 100  $\mu$ m. The CasaXPS programme was employed in the analysis of XPS data. Proton NMR spectra were recorded on a 400 MHz Bruker Ultrashield spectrometer at room temperature using deuterated CDCl<sub>3</sub> or DMSO as solvents. The Suzuki–Miyaura coupling reactions and solventfree oxidation of benzyl alcohol products were identified using GC-FID (Shimadzu 2010 gas chromatograph).

### General procedure for Suzuki reaction

In a typical Suzuki reaction, phenylboronic acid (2.5 mmol), aryl halide (2.5 mmol), Pd catalysts (20 mg), K<sub>2</sub>CO<sub>3</sub> (4 mmol) and EtOH–H<sub>2</sub>O (1:1, v/v, 10 mL) solvents were added into a round-bottom flask equipped with a stirrer. The reaction mixtures were stirred at 60 °C for 10–30 min under reflux. Upon reaction completion, the reaction product was cooled and filtered through a 0.22- $\mu$ m pore polycarbonate filter to separate the catalyst, and the filtrate was extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL) three times. The organic layer fractions were combined into one conical flask and dried with anhydrous sodium sulphate. Thereafter, the mixture was filtered, and the residue was concentrated by flash chromatography on silica gel (0.0063–0.20 mm) with hexane/ethyl acetate (10:1) eluent, leading to isolation of pure biphenyl product.

### Solventfree oxidation of benzyl alcohol

The solventfree oxidation reactions of benzyl alcohol were carried out in a three-necked round-bottom flask (25 mL), pre-heated in an oil bath equipped with a condenser. Pd catalysts (20 mg) was added to benzyl alcohol (5.0 mL) and stirred at 500 rpm for each experiment. The mixture was heated under reflux at 110 °C for 3 h and flushed with pure oxygen at a flow rate of 20 mL/min. After the reaction, the products were cooled to room temperature and centrifuged to separate the catalysts. The products were analysed by a 30-m DB-1 capillary gas chromatography (GC) equipped with FID detector (Shimadzu 14B, FID detector) using n-dodecane as an internal

standard. The column temperature was kept at 100 °C for 10 min and then raised to 200 °C at a heating rate of 10 °C/min. The conversion of benzyl alcohol and selectivity towards benzaldehyde product was calculated after three consecutive runs. The turn over frequency (TOF) for each catalyst was calculated using Eq. (1).

$$\text{TOF} = \frac{\text{No. of moles of BZA}}{\text{No. of moles of active centres on catalyst} \times \text{time(h)}} \quad (1)$$

### Recycling and hot filtration leaching tests

After each catalytic cycle, the catalyst was firstly washed sufficiently with distilled water, sequentially with ethanol and acetone and then finally with dichloromethane before being dried at 110 °C for 24 h. Further catalytic reaction was carried out using the dried black residue. Hot filtration leaching test was carried out for the Suzuki reaction between iodobenzene (2.5 mmol) and phenylboronic acid (2.5 mmol) under optimized conditions. After 30 min, half of the reaction mixture was centrifuged and filtered while hot at 2000 rpm. The reaction was allowed to continue under stirring for another 6 h. Subsequently, the reaction yield of the unfiltered and the filtered solution was monitored by GC analysis after sampling at a predetermined time.

## Results and discussion

### Characterization of catalysts

The structural information and the crystalline phase of the catalysts were investigated using an X-ray diffractometer. Figure 1a shows the XRD pattern of Pd/CNTs, Pd/N-CNTs and Pd/N-CNTs-1%. All the catalyst showed the diffraction characteristic peaks of Pd NPs. The diffraction peak at 26.35° was indexed to the (002) crystal face reflection of the graphitic carbon in CNTs and N-CNTs, while the peaks at 40.00, 46.75 and 68.18° were attributed to the (111), (200) and (220), respectively, hexagonal close-packed crystalline phase of Pd face-centred cubic (fcc) structure in Pd/N-CNTs and Pd/CNTs [49].

The Pd NPs crystallite sizes were estimated from Pd (111) peaks using the Scherrer equation given in Eq. (2):

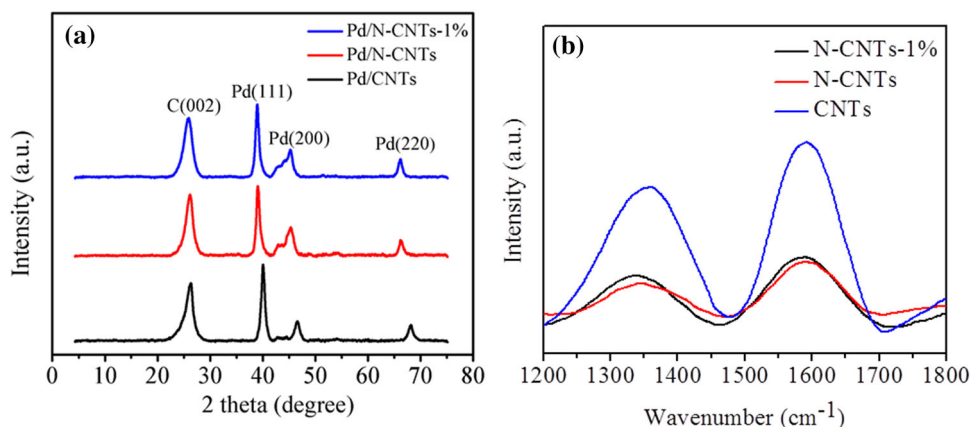
$$D = \frac{0.89\lambda}{\beta \cos \theta} \quad (2)$$

where  $D$  = average diameter of the Pd/NPs in nm,  $\lambda = 0.154$  nm (i.e. the wavelength of the X-rays),  $\theta$  = diffraction angle of the Pd (111) reflection and  $\beta$  = full width at half maximum (FWHM) of the Pd reflection plane. The lattice  $d$ -spacing calculated for the Pd (111) plane by Bragg's law for Pd/CNTs, Pd/N-CNTs and Pd/N-CNTs-1% was found to be 2.3152, 2.2530 and 2.3917 Å, respectively. According to the Scherrer's method, the full width at half maximum (FWHM) of the diffraction peak is inversely proportional to the particle size [50]. The calculated palladium nanoparticle sizes of Pd/CNTs, Pd/N-CNTs and Pd/N-CNTs-1% were 9.5, 3.1 and 7.5 nm, respectively. This trend is comparable with the nanoparticle size obtained from the TEM analysis (Table 1). The ICP-OES analysis of the catalysts gave approximately 0.02 mol% Pd loading for all catalysts (Table 1).

The carbon framework and structural defect instigated by N-doping was further evaluated quantitatively by the Raman spectroscopy (Fig. 1b). This was done to evaluate the degree of disordered carbon structure caused by a defect on the graphitic carbon sheets. An intense D-band peak at  $\sim 1348$   $\text{cm}^{-1}$  and G-band at  $\sim 1590$   $\text{cm}^{-1}$  are ascribed to the disordered carbon and the graphitic carbon, respectively [51]. The ratio of D- to G-band intensity ( $I_D/I_G$ ) was used to estimate the degree of distortions that exist in CNTs and N-CNTs. It was found that the ratio of  $I_D/I_G$  for Pd/CNTs (0.7583) was much less when compared to Pd/N-CNTs (0.9738) and Pd/N-CNTs-1% (0.8366). The lower  $I_D/I_G$  ratio demonstrates a more graphitic structure for Pd/CNTs, while on the other hand higher  $I_D/I_G$  ratio suggests a more successful N-doping in the increasing order of Pd/N-CNTs to Pd/N-CNTs-1%.

The SEM images of the Pd/N-CNTs showed a uniformly dispersed spherical Pd NPs indicative of a hierarchical porous network, often required in heterogeneous catalysis [52] (Fig. 2a). The morphology and the deposition of Pd NPs on CNTs and N-CNTs were clearly identified by the dark spots visible in Fig. 2b, c, respectively. Figure 2b, c shows a typical TEM and HRTEM images of Pd/N-CNTs-1%.

**Figure 1** **a** XRD diffraction pattern and **b** Raman spectra of Pd/CNTs, Pd/N-CNTs and Pd/N-CNTs-1% catalysts.

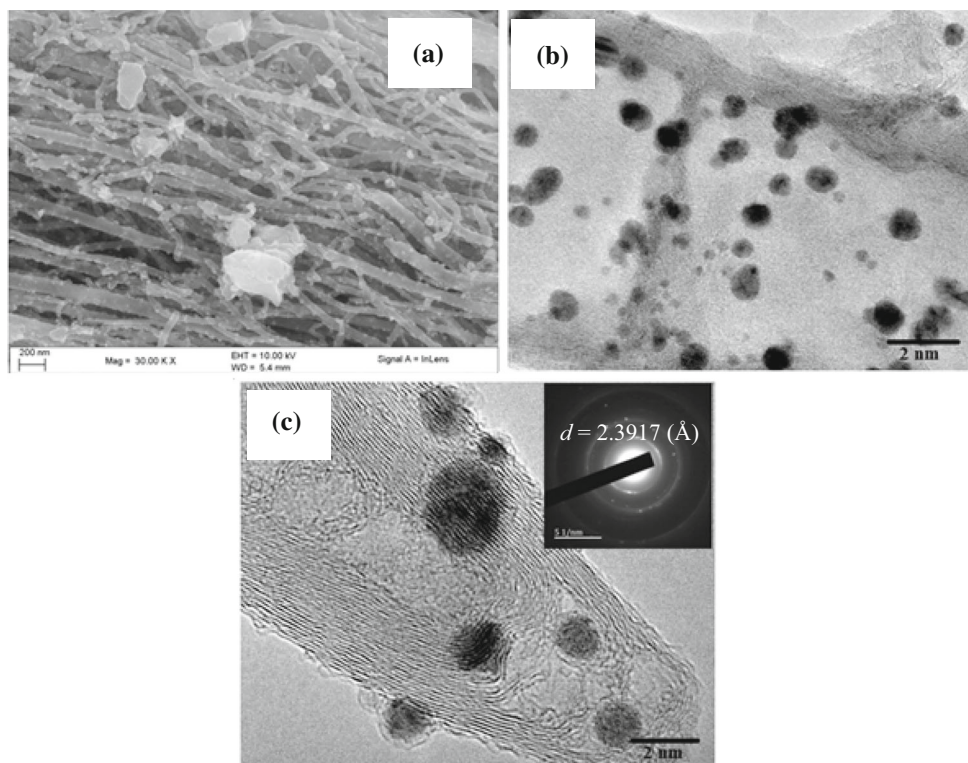


**Table 1** Properties of Pd/CNTs and Pd/N-CNTs catalysts based on ICP-OES, XRD and TEM

Entry	Catalyst	XRD			TEM $d_{\text{NP}}/\text{nm}^{\text{b}}$	(ICP-OES) Pd loading (mol%) <sup>c</sup>
		$d_{\text{NP}}/\text{nm}^{\text{a}}$	Interlayer spacing (Å)	FWHM of Pd (111) peak (°)		
1	Pd/N-CNTs	3.1	2.2530	0.2519	3.4	0.016
2	Pd/N-CNTs-1%	7.5	2.3917	0.2519	7.3	0.019
3	Pd/CNTs	9.10	2.3152	0.2340	8.7	0.017

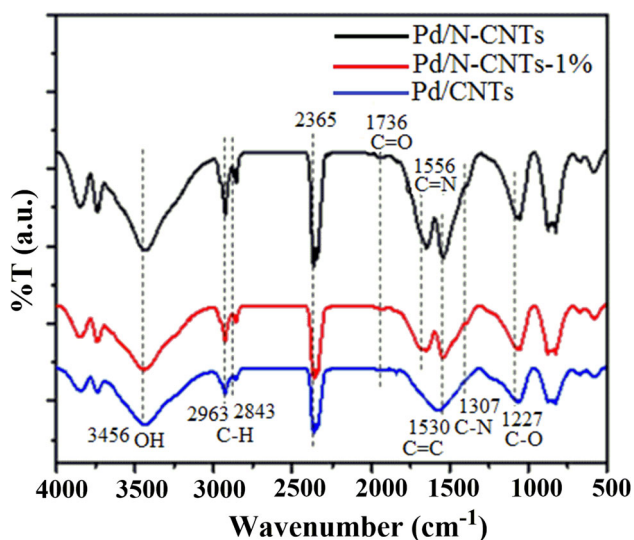
<sup>a</sup> $d_{\text{NP}}$ —palladium nanoparticle diameter size determined by powdered XRD; <sup>b</sup> $d_{\text{NP}}$ —palladium nanoparticle diameter size determined by TEM; <sup>c</sup>mol% of Pd on N-CNTs determined by ICP-OES

**Figure 2** **a** SEM image of the Pd/N-CNTs-1%, **b** TEM image of Pd/N-CNTs-1% and **c** HRTEM image of Pd/N-CNTs-1%. Inset shows the matching SAED patterns.



TEM investigations revealed the average sizes to be 3.4, 7.3 and 8.7 nm, for CNTs, N-CNTs and N-CNTs-1%, respectively, and it also showed the distribution of the embedded Pd NPs. This result is consistent with particle sizes reported by Wang et al. [35]. Notably, the density of Pd NPs on N-CNTs-1% is profuse, and no nanoparticle aggregation is observed on the nanotube surface (Fig. 2b). The TEM result indicates that N-doping plays an essential role in Pd NPs dispersibility due to close interaction between Pd particles and defective N-CNTs than the graphitic CNTs [53]. The Pd atoms are deposited on the curvature of the wrinkled carbon sheets (Fig. 2c), suggestive of a functional interaction between Pd NP and N atom on N-CNT structure [53]. The crystallinity of Pd NPs anchored on the graphitic carbon was further determined by a selective area electron diffraction pattern (SAED, inset in Fig. 2c). The *d*-spacing (2.3917 Å) is consistent with the Pd (111) planes obtained from XRD analysis. Pd NPs consists of concentric rings, composed of bright discrete diffraction spots, which can be indexed to the (111), (200), (220) and (311) planes of fcc Pd. The SAED pattern of the as-prepared Pd nanoparticles shows their high crystallinity.

The chemical composition was investigated by FTIR (Fig. 3). The peaks at 2963 and 2843  $\text{cm}^{-1}$  characterize the stretching vibration of the  $\text{CH}_2$  and  $\text{CH}_3$  groups, respectively, present in all samples [54]. The bands at 1530 and 1307  $\text{cm}^{-1}$  are assigned to the  $\text{sp}^2$  C=C and aromatic C–N stretching bonds,



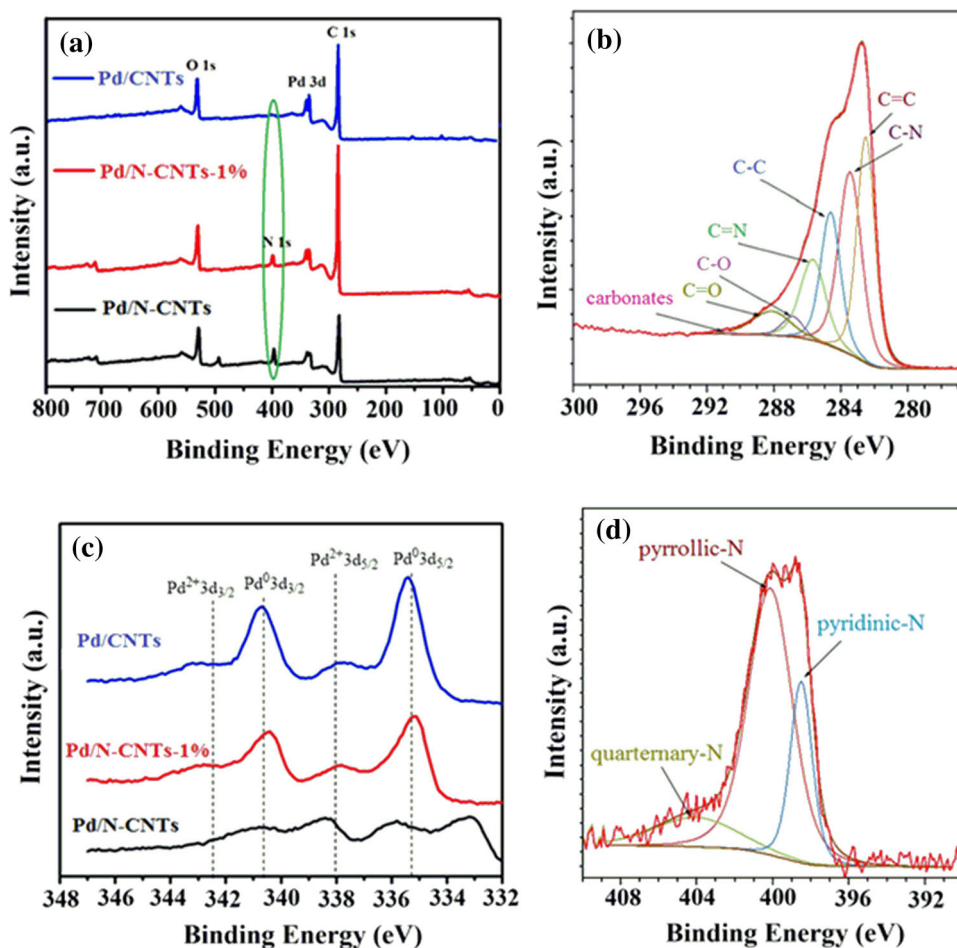
**Figure 3** FTIR spectra of Pd/CNTs, Pd/N-CNTs and Pd/N-CNTs-1%.

respectively [55]. The bands at 1736, 1556 and 1227  $\text{cm}^{-1}$  were assigned to C=O, C=N and C–O, respectively [56–58]. The peak observed at 2370  $\text{cm}^{-1}$  was assigned to trapped  $\text{CO}_2$  stretching and was observed in all samples [56, 59]. Compared with Pd/CNTs, the appearance of C=N and C–N functional groups in Pd/N-CNTs indicates the doping of N atom into the graphitic carbon.

The bulk composition of Pd/CNTs, Pd/N-CNTs and Pd/N-CNTs-1% catalysts was analysed with an X-ray photoelectron spectroscopy (XPS). The full spectra survey (Fig. 4a) revealed the presence of C, O and Pd in Pd/CNTs, while C, N, O and Pd were detected in Pd/N-CNTs. The percentage composition of all surface elements from XPS analysis is given in Supplementary Table S1. C 1s peaks were deconvoluted into five individual peaks as shown in Fig. 4. The robust signals C 1s confirmed the presence of oxygen functionalization on the CNTs and N-CNT surfaces. Figure 4b shows the peaks at 286.6 (C–O), 288.7 (O–C=O) and 290.2 eV (C–O–C), which are ascribed to the oxygen-containing moieties [45, 60, 61]. The peaks 284.3, 285.1, 287.1, 283.9 and 291.5 eV are assigned to  $\text{sp}^2$  C,  $\text{sp}^3$  C, C=N, C–N and carbonates, respectively.

The total nitrogen content on N-CNTs and N-CNT-1% was 10.56 and 6.92 at.%, respectively (Supplementary Table S1). A similar result was reported by Koos et al. [62], where nitrogen contents in N-CNTs decrease as N/C ratio decreases. The N 1s peaks of the high-resolution spectrum (Fig. 4d; Supplementary Figure S5) were deconvoluted to three symmetrical peaks assigned to pyridinic (398.4 eV), pyrrolic (400.1 eV) and oxidized nitrogen-like N-oxides of pyridinic-N (404.2 eV) which is typical of N-doped CNTs [63, 64]. The analysis of the N 1s spectra conformed with Kotakoski et al. [65] simulation, which suggested that at higher nitrogen atom concentration, N atom might be introduced as pentagon defect corresponding to pyrrolic-N type, while incorporation of a lower amount of nitrogen into the CNTs hexagonal structure was ascribed to pyridinic-N type [66]. Although most studies argue that the type of nitrogen functionalities and N-doping level can be controlled or rather depend on synthesis condition [67–70], the introduction of oxygen-containing benzophenone into the reaction mixture can lead to substantial increase in the pyrrolic-N. This can be attributed to the formation of  $\text{NO}_x$  resulting from the reaction of nitrogen with oxygen. On the other hand,

**Figure 4** **a** XPS survey scan spectra of the three Pd catalysts, **b** C 1s spectrum of Pd/N-CNT-0%, **c** Pd 3d spectrum of the three Pd catalysts and **d** N 1s spectrum of Pd/N-CNT-1%.



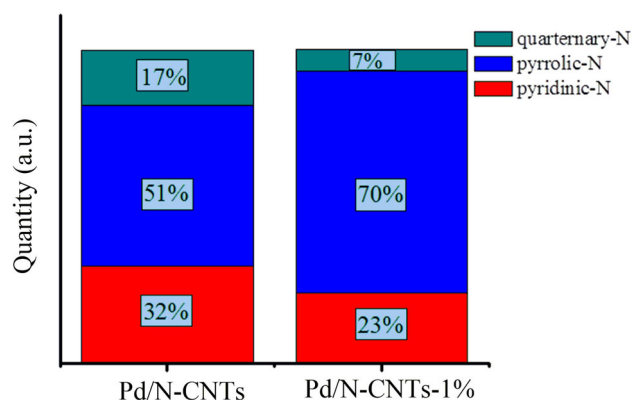
also the emergence of pyridinic oxides is a result of the conversion of quaternary-N. This occurs due to highly reactive oxidation reaction induced by the presence of benzophenone dissolved in the reaction mixture for N-CNTs-1% [71].

XPS analysis also showed the chemical state of Pd particles on CNTs and N-CNTs surface. The interaction of the pyrrolic nitrogen of N-CNTs and Pd NPs of different sizes showed pairs of doublet overlapping peaks in Pd 3d XPS spectra, corresponding to Pd 3d<sub>5/2</sub> and Pd 3d<sub>3/2</sub> (Fig. 4c). The Pd 3d peaks with binding energies at 335.6 eV (Pd<sub>5/2</sub>) and 340.6 eV (Pd<sub>3/2</sub>) [72, 73] were attributed to Pd<sup>0</sup>, while peaks at 337.7 eV (Pd<sub>5/2</sub>) and 342.7 eV (Pd<sub>3/2</sub>) [74] were related to Pd<sup>2+</sup> (Supplementary Table S2). The XPS data also revealed that Pd<sup>0</sup> was predominant on the surfaces of the three catalysts with no noticeable Pd<sup>2+</sup> ion, indicating that Pd<sup>2+</sup> ion was reduced to Pd NPs. The weak Pd<sup>2+</sup> peak observed at 336.3–336.9 eV was attributed to the formation of PdO due to sample exposure to air. The deposited Pd NPs were well

anchored on N-CNTs with an average size of 3.4 and 7.3 nm for N-CNTs and N-CNTs-1%, respectively. This could be attributed to the high nitrogen density on the N-CNTs surface and enhanced anchoring of the Pd NPs, making the catalysts less prone to agglomeration and sintering on cooling during catalyst synthesis. Following the peak area integration of Pd 3d peaks, the total molar fraction of Pd is ~ 76% for Pd/N-CNTs, while Pd/N-CNTs-1% had a lower value of 56%. Detailed XPS results are accessible in Supporting Information Table S1 and Table S2.

For N-CNTs, the decrease in the pyridinic-N concentration with increased pyrrolic-N was observed upon introduction of oxygen into the reaction mix (Fig. 5; Supplementary Table S1). It is noteworthy that pyrrolic-N species were 70% in Pd/N-CNTs-1%, with such N species acting as anchoring site, thereby enabling the nucleation and growth of metal nanoparticles [75]. From the results, the increased percentage of pyrrolic-N is due to the dilution of the nitrogen source which largely affects the N species





**Figure 5** Distribution of nitrogen species (%) present in Pd/N-CNTs and Pd/N-CNTs-1%.

formation [76, 77]. Also, the observed increase in pyrrolic-N concentration for N-CNTs-1% could be attributed to the decrease in  $N/C$  ratio in the reaction mixture as precursor decomposition is assumed to occur at the surface of Fe NPs (i.e. top-growth model) [78]. The formation of pyrrolic-N and pyridinic-N on the outer shell of N-CNTs is due to the interaction of NH and CN species on catalyst surface followed by their surface or subsurface diffusion [79].

The surface area properties of the synthesized Pd/CNTs, Pd/N-CNTs and Pd/N-CNTs-1% catalysts were obtained from  $N_2$  adsorption–desorption isotherms as given in Table 2 with the typical isotherm shown in Fig. 6a. All samples showed type IV isotherm curves [80] with an  $H_1$  hysteresis loop between 0.50 and 0.99 P/Po, typical of mesoporous and macroporous structured material with narrow pore size distribution associated with a cylindrical-like porous material such as CNTs [81]. The oxidation of the CNTs and N-CNTs via acid treatments led to the opening of tube ends, which upon deposition of Pd metal, these openings were blocked by nanoparticles, thereby inhibiting  $N_2$  adsorption. This results in a

**Table 2** Surface area of catalyst support used

Catalyst	$S_{BET}$ ( $m^2g^{-1}$ )	Pore volume distribution (nm)
CNT	135.42	0.434
N-CNTs	55.29	1.031
N-CNTs-1%	98.46	0.736
Pd/CNTs	133.87	0.402
Pd/N-CNTs	47.44	1.361
Pd/N-CNTs-1%	87.50	0.846

decrease in the surface area of Pd/CNTs ( $133.87 m^2g^{-1}$ ), Pd/N-CNTs ( $47.44 m^2g^{-1}$ ) and Pd/N-CNTs-1% ( $87.50 m^2g^{-1}$ ) catalysts [82, 83], relative to plain CNTs ( $135.42 m^2g^{-1}$ ), N-CNTs ( $55.29 m^2g^{-1}$ ) and N-CNTs-1% ( $98.46 m^2g^{-1}$ ), respectively. A significant increase in surface area was observed for N-CNTs-1% upon introduction of benzophenone in the reaction mixture, due to increase porosity caused by oxygen activation of the disordered N-CNTs.

Pd/N-CNTs showed the highest pore volume of 1.361 nm followed by Pd/N-CNTs-1% (0.846 nm) and Pd/CNTs (0.402 nm) (Fig. 6b), which could be associated with variation in reactant stoichiometry and post-synthesis functionalization [84, 85].

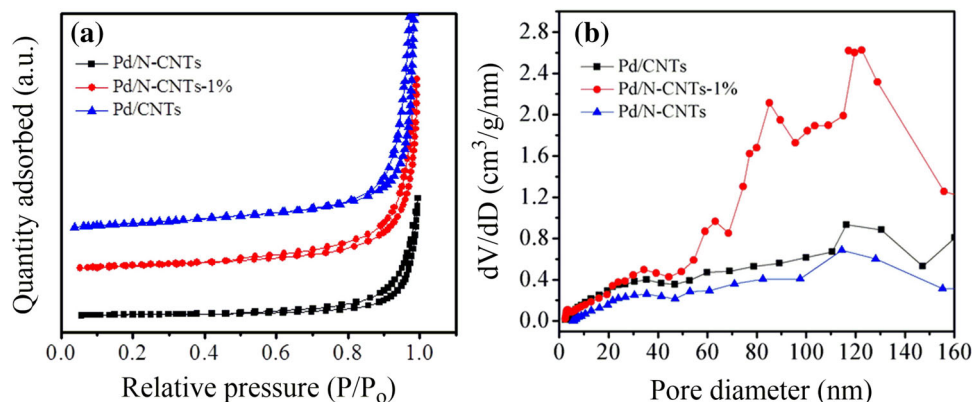
The strong interaction between CNTs (and N-CNTs) support and Pd NPs stabilization was investigated by  $H_2$ -TPR (Supplementary Figure S4). This interaction is evidenced by the reduction in temperature observed for the three catalysts in the  $H_2$ -TPR experiment. The position, width and intensity of the peaks depend significantly on the carbon material synthesis and pre-treatment of the supports. From the  $H_2$ -TPR profile, the hydrogen desorption peak at 50 °C could be attributed to interstitial Pd  $\beta$ -hydride. A sharp peak centred at 298 °C can be observed from Pd/CNTs and Pd/N-CNTs (Supplementary Fig. 4). The broad peak centred at 120 °C could be ascribed to the reduction of  $Pd^{2+}$  to  $Pd^0$  which is in support of observed results from the Pd 3d XPS spectra [86] (Fig. 5c).

## Catalytic performance

### Suzuki coupling reactions

A typical Suzuki coupling reaction was conducted using iodobenzene (2 mmol) and phenylboronic acid (2.5 mmol) as reactants, a base (4 mmol) and catalyst (20 mg). The solvent, base and temperature were varied to optimize the reaction conditions (Table 3). Table 3 summarizes the results obtained for quantitative yields of biphenyl compounds. High yields were obtained in protic solvents such as MeOH, EtOH and iPrOH (Table 3, entries 1, 2 and 12), while poor yields were obtained for aprotic solvents such as DMF, dioxane, acetonitrile and acetone (Table 3, entries 11 and 13–15). However, when  $H_2O$  was introduced as a solvent, a gradual increase in reactivity was observed relative to aprotic solvents

**Figure 6** **a** N<sub>2</sub> adsorption–desorption isotherms and **b** pore size distribution of Pd/CNTs, Pd/N-CNTs and Pd/N-CNT-1%.



**Table 3** Screening of the reaction conditions for Suzuki cross-coupling reactions of phenylboronic acid with iodobenzene catalysed by Pd/N-CNTs

Entry	Solvents	Base	Temperature (°C)	Yield <sup>a</sup> (%)
1	MeOH	K <sub>2</sub> CO <sub>3</sub>	60	85
2	EtOH	K <sub>2</sub> CO <sub>3</sub>	60	86
3	H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	60	59
4	H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	100	65
5	THF–H <sub>2</sub> O (1:1, v/v)	K <sub>2</sub> CO <sub>3</sub>	80	46
6	EtOH–H <sub>2</sub> O (1:1, v/v)	K <sub>2</sub> CO <sub>3</sub>	60	98
7	EtOH–H <sub>2</sub> O (1:1, v/v)	NaOAc	60	80
8	EtOH–H <sub>2</sub> O (1:1, v/v)	Na <sub>2</sub> CO <sub>3</sub>	60	92
9	EtOH–H <sub>2</sub> O (1:1, v/v)	Et <sub>3</sub> N	60	82
10	EtOH–H <sub>2</sub> O (1:1, v/v)	K <sub>2</sub> PO <sub>4</sub>	70	67
11	DMF	K <sub>2</sub> CO <sub>3</sub>	80	27
12	iPrOH	K <sub>2</sub> CO <sub>3</sub>	80	82
13	Dioxane	K <sub>2</sub> CO <sub>3</sub>	80	26
14	CH <sub>3</sub> CN	NaOH	80	34
15	Acetone	K <sub>2</sub> CO <sub>3</sub>	80	46

Reaction conditions: iodobenzene (2 mmol) was reacted with phenylboronic acid (2.5 mmol) in the presence of a base (2 mmol) for 20 min, 20 mg of Pd/N-CNTs catalyst

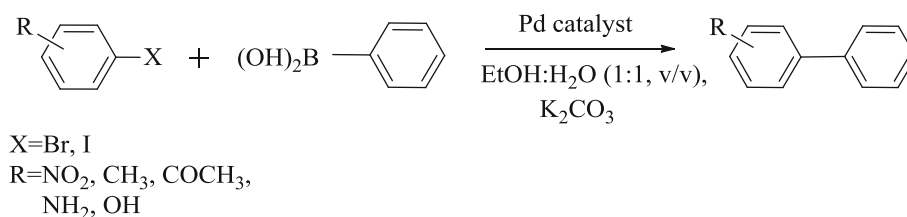
<sup>a</sup>Yields were calculated after isolation of the pure biphenyl compound through short-column chromatography using silica gel (100–200 mesh)

(Table 3, entry 3). An increase in the reactant solubility and reactivity was observed when solvent mixtures were employed (i.e. EtOH–H<sub>2</sub>O (1:1 v/v, 10 mL) and THF–H<sub>2</sub>O (1:1 v/v, 10 mL)) (Table 3, entries 5–10) similar to previous reports [87].

The advantage of the solvent mixture could be ascribed to the better solubility of the organic reactant in the organic base, which activates the phenylboronic acid and promotes reductive elimination reactions [88]. EtOH–H<sub>2</sub>O was found to be the solvent of choice than various bases such as K<sub>2</sub>CO<sub>3</sub>, NaOAc, KOH and Et<sub>3</sub>N. K<sub>2</sub>CO<sub>3</sub> produces better yields compared to Na<sub>2</sub>CO<sub>3</sub>, NaOAc and Et<sub>3</sub>N bases. This could be attributed to the partial homogeneity of K<sub>2</sub>CO<sub>3</sub> in the aqueous phase, leading to effective

activation of phenylboronic acid towards boronate complex formation [89]. The yield noticeably reduced from 92 to 82% for Na<sub>2</sub>CO<sub>3</sub> and Et<sub>3</sub>N, respectively (Table 3, entries 8 and 9).

Using the obtained optimum conditions, the catalytic efficiency of Pd catalysts in the coupling reaction between aryl halides (such as I and Br) and phenylboronic acid was investigated (Table 4). The reactions were rapid from 60 to 100 °C, beyond which an increase in the temperature did not increase the yield. Substituted aryl halide substrates with electron-withdrawing groups (–NO<sub>2</sub>, –COCH<sub>3</sub> and –CF<sub>3</sub>) and electron-donating groups (–CH<sub>3</sub>, –H and –NH<sub>2</sub>) produced good yields ranging from 73 to 98% of biphenyl compounds. The highest yield with

**Table 4** Catalytic performance of different supported Pd-based catalysts for Suzuki cross-coupling reaction under optimized conditions

Entry	Aryl halide	Time (min)	Yields <sup>a</sup> (%)		
			Pd/CNTs	Pd/N-CNTs	Pd/N-CNTs-1%
1	H-C <sub>6</sub> H <sub>4</sub> I	20	83	89	97
2	4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> I	20	76	86	97
3	4-OH-C <sub>6</sub> H <sub>4</sub> I	15	65	82	94
4	4-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> I	20	58	65	92
5	4-COCH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> I	20	71	85	94
6	4-NH <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> Br	20	83	86	98
7	H-C <sub>6</sub> H <sub>4</sub> Br	20	89	91	98
8	4-OH-C <sub>6</sub> H <sub>4</sub> Br	20	88	91	99
9	4-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> Br	20	86	92	93
10	4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> Br	20	86	82	96
11	2-I-C <sub>6</sub> H <sub>4</sub> COOH	20	25	36	76
12	2-OH-C <sub>6</sub> H <sub>4</sub> Br	20	65	68	97
13	2-COCH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> Br	20	65	45	83
14	2-CF <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> I	15	84	68	91

Reaction conditions: aryl halide (2 mmol), phenylboronic acid (2.5 mmol), K<sub>2</sub>CO<sub>3</sub> (4 mmol), catalyst (20 mg) and EtOH-H<sub>2</sub>O (1:1, v/v, 10 mL) at reflux 60 °C under air

<sup>a</sup>Isolated yields based on aryl halides. Under the equation, Pd catalyst refers to Pd/CNT, Pd/N-CNTs or Pd/N-CNTs-1% as catalyst used

substituted aryl bromide was obtained using Pd/N-CNTs-1% catalyst within 10–30 min (Table 4, entries 2–10). Effect of substituents on the aryl halide has been reported for Suzuki reactions [90]. The lower yield obtained for electron-withdrawing substituent (–COOH) which facilitates the rate-limiting oxidative reaction could be attributed to increased acidity in the reaction mixture [90] (Table 4, entry 11). The sterically hindered *ortho*-substituted 2-bromophenol and 2-iodobenzotrifluoride proceeded with good yields but not with excellent yields as obtained for *para*-substituted aryl halide (Table 4, entries 12 and 14). Among substituted aryl halides, substituted bromobenzene gave higher yields (Table 4, entry 10) than substituted iodobenzene (Table 4, entry 2), even though iodobenzene shows greater reactivity than bromobenzene due to iodine being a better leaving group. Nonetheless, there are known exceptions where reverse catalytic activity was observed for alkyl iodide as a substrate for Suzuki coupling

reactions. This could be attributed to the generation of iodide anion (I<sup>−</sup>) from alkyl iodide acting as a catalyst inhibitor during the catalytic reaction [91]. The excellent catalytic activity of Pd/N-CNTs-1% over Pd/N-CNTs and Pd/CNTs could be attributed to the smaller particles size of Pd NPs [92–94] and the strong interaction between Pd NPs and pyrrolic-N atom incorporated in the graphitic *sp*<sup>2</sup> carbon, thereby preventing Pd leaching and agglomeration. From the results of TEM sample measurements (from images obtained) and values calculated from Scherrer equation, XRD (Table 1), the order of Pd particle size on CNTs, N-CNTs and N-CNTs-1% supports follows the order Pd/CNTs < Pd/N-CNTs-1% < Pd/N-CNTs, respectively. The yield of biphenyls obtained follows the order Pd/CNTs < Pd/N-CNTs < Pd/N-CNTs-1%. The inconsistency in the particle size trend and the yield suggest that the Suzuki coupling reaction was influenced not only by the change in particle sizes but by other factors such as surface properties

and the nature of the support (amount of pyrrolic-N atom, XPS analysis) [33].

The efficiency of Pd/N-CNTs and Pd/N-CNTs-1% catalysts in this work is compared to those reported elsewhere for Suzuki coupling reactions of bromobenzene and phenylboronic acid [37, 38]. Table 5 shows that all reactions proceeded with better yields (> 90%) except a few with harsh reaction conditions and longer reaction times. From BET analysis, the surface area of Pd/CNTs, Pd/N-CNTs and Pd/N-CNTs-1% catalysts follows the order Pd/CNTs > Pd/N-CNTs-1% > Pd/N-CNTs. However, it was found that the yield of biphenyl follows the order Pd/CNTs < Pd/N-CNTs < Pd/N-CNTs-1%. This suggests that the coupling reaction is dependent not only of the surface area but also other factors such as surface properties including the pore volume [95, 96] and the nature of the support (amount of pyrrolic-N atom) [33].

### Solventfree benzyl alcohol oxidation reactions

In our study, we extend the application of Pd/CNTs, Pd/N-CNTs and Pd/N-CNTs-1% catalysts in the solventfree oxidation reaction of benzyl alcohol. The catalytic activities of the Pd catalysts in the oxidation of benzyl alcohol in pure oxygen with a flow rate of 20 mL/min at a temperature of 110 °C were investigated. A blank reaction without any catalyst was conducted. A lower conversion of 3% (Table 6) was obtained, confirming that the reaction could not proceed in the absence of a catalyst. Also, the use of CNTs and N-CNTs as catalysts produced noticeable

conversions of 15 and 35%, respectively (Fig. 7a). The oxidation reaction continued progressively as the catalytic activities increased in the order Pd/N-CNTs-1% > Pd/N-CNTs > Pd/CNTs, which correlates with an increase in the pyrrolic-N atom as observed in the XPS results. This increased catalytic activity is attributable to the effective enhancement of active surface oxygen by Pd NPs. For Pd/N-CNTs-1% and Pd/N-CNTs, about 98 and 96% conversion was achieved after 2 h of reaction, respectively, with a high TOF (Table 6). Nonetheless, a lower conversion was obtained for Pd/CNTs which could be due to the resulting agglomeration of Pd NPs which led to unfavourable larger Pd NPs size. The selectivity of Pd/N-CNTs-OT catalyst (96%) was found to be superior to Pd/N-CNTs which is reported in the literature [35] with larger particle size (Table 7, entries 5 and 7).

The catalytic strength of our catalyst for benzyl alcohol oxidation is comparable to other reported Pd-catalysed reactions (Table 7). The low selectivity observed for Pd/CNTs, Pd/N-CNTs and Pd/N-CNTs-1% catalysts after 30 min of reaction (Fig. 7b) is a result of (1) initial hydrogenolysis of benzyl alcohol towards the formation of toluene and (2) parallel oxidation reaction between benzyl alcohol and hydrogen [30]. However, further reaction of oxygen with hydrogen suppresses the hydrogenolysis reaction, thereby enhancing selectivity towards benzaldehyde formation after 120 min.

**Table 5** Catalytic performances of some Pd-based catalysts for Suzuki coupling of bromobenzene and phenylboronic acid

Entry	Catalyst	Reaction conditions (solvent, base, temp, time, Pd loading)	Yield (%)	TOF (h <sup>-1</sup> )	Refs.
1	CMC-NHC-Pd	EtOH-H <sub>2</sub> O, K <sub>2</sub> CO <sub>3</sub> , 60 °C, 3 h, 0.8 mol%	96	120	[97]
2	MOF-NPC-Pd	EtOH-H <sub>2</sub> O, K <sub>2</sub> CO <sub>3</sub> , 78 °C, 1 h, 0.1 mol%	98.6	–	[98]
3	Pd-rGO	EtOH-H <sub>2</sub> O, NaOH, 60 °C, 24 h, 0.5 mol%	5	0.4	[99]
4	Schiff base-MCNT-Pd	EtOH-H <sub>2</sub> O, K <sub>2</sub> CO <sub>3</sub> , r.t, 1 h, 0.2 mol%	98	–	[100]
5	G-MWCNTs-Pd	EtOH-H <sub>2</sub> O, K <sub>2</sub> CO <sub>3</sub> , 60 °C, 1 h, 0.5 mol%	95	799	[87]
6	Isoniazole-MWCNT-Pd	EtOH-H <sub>2</sub> O, K <sub>2</sub> CO <sub>3</sub> , 60 °C, 2 h, 0.2 mol%	98	–	[101]
7	Pd/CNT	H <sub>2</sub> O, Na <sub>2</sub> CO <sub>3</sub> , 80 °C, 24 h, 0.01 mol%	97	40	[102]
8	Pd@PANI	EtOH, K <sub>2</sub> CO <sub>3</sub> , 78 °C, 24 h, 0.12 mol%	76	–	[103]
9	Pd/N-CNTs	EtOH-H <sub>2</sub> O, K <sub>2</sub> CO <sub>3</sub> , 60 °C, 0.25 h, 0.02 mol%	91	2050	This work
10	Pd/N-CNTs-1%	EtOH-H <sub>2</sub> O, K <sub>2</sub> CO <sub>3</sub> , 60 °C, 0.25 h, 0.02 mol%	98	1068	This work

**Table 6** Catalytic performance of Pd/CNTs and Pd/N-CNTs catalyst in solventfree selective oxidation of benzyl alcohol

Samples	Conversion (%)	Selectivity (%)	TOF(h <sup>-1</sup> )
No catalyst	< 3	< 4	–
CNTs	15 ± 0.8	85 ± 2.7	247
N-CNTs	38 ± 2.6	94 ± 1.9	614
Pd/CNTs	85 ± 1.8	65 ± 0.2	9349.5
Pd/N-CNTs	96 ± 0.2	80 ± 0.1	10560
Pd/N-CNTs-1%	98 ± 0.1	96 ± 0.5	10780

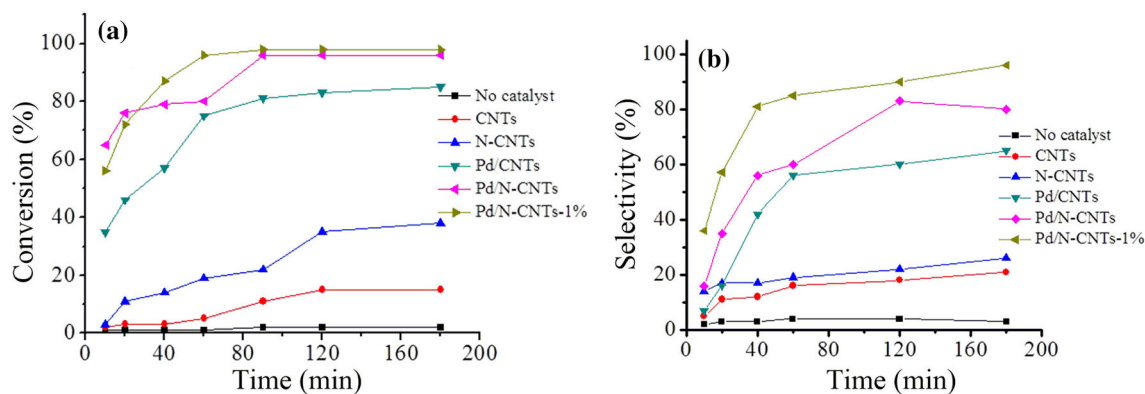
Reactions condition: 5 mL benzyl alcohol, 110 °C, 3 h, 50 mg catalyst, molecular O<sub>2</sub>. Conversion = mmol (benzyl alcohol) converted/mmol (initial benzyl alcohol) × 100%. Selectivity of benzaldehyde (%) = measured [benzaldehyde]/measured [benzyl alcohol converted] + measured [other products] × 100%

### Influence of the catalyst preparation conditions on catalytic performance

From our experiments, it has been shown that N-CNTs and N-CNTs-1% are more efficient support than CNTs for Pd-catalysed reactions. For N-CNT, nitrogen atom usually increases the electron density on metal catalysts, thereby providing a suitable site for anchoring [71], leading to better dispersion and ultimately facilitating the adsorption of reactant and desorption of products [108–110]. The lone pair bonding electron and higher electronegativity of the substituted N atoms within the carbon support enhance the support basicity, hence promoting the desorption of nitrogen at low temperature [111]. Also, nitrogen doping modifies the Pd NPs active sites. During catalyst preparation, active Pd NPs crystallites react with both the pyrrolic- and the pyridinic-N atoms on nanotubes surfaces. We also presume that nitrogen atoms are uniformly spread inside the nanotubes.

The introduction of oxygen during the carbon support synthesis and chemical functionalization offers great opportunities in tailoring the surface properties of these materials with better porosity, thereby enhancing diffusion and mass transfer of substrates during catalytic reactions [112]. The presence of hydrogen decreases the amount of N atoms doped on CNTs due to the reaction of N and H radicals to form NH<sub>3</sub> and HCN gases [113]. We, therefore, concluded that oxygen played a vital role by improving the nanotubes' quality by scavenging the H radicals via the reaction (i.e. H + O<sub>2</sub> → OH + O), as evidenced by the presence of a strong OH band obtained for N-CNTs-1% from the FTIR analysis (Fig. 4). The formation of OH radicals subsequently helps to suppress carbon etching at the growing edges, remove amorphous carbon (i.e. C + O → CO + O → CO<sub>2</sub>) and limit the supersaturation of carbon molecule during N-CNTs growth.

Surface properties of the CNTs and N-CNTs can be influenced by the amount of C–O functional group and the metal particle size. The Pd NPs size distribution on CNTs, N-CNTs and N-CNTs-1% is shown in Supplementary Figure S1. The Pd NPs size on the carbon materials follows the order: Pd/CNTs > Pd/N-CNTs > Pd/N-CNTs-1%. N-CNTs-1% produce good Pd particle dispersion due to the presence of a carbonyl functional group on the carbon surface. This was confirmed by O 1s peak of the three fitted components in the samples, namely: quinone and carbonyl group (C=O, 531.15 eV) [114]; ether and hydroxyl oxygen (C–O, 533.4 eV) [115, 116]; and carboxylic group oxygen (COOH, 534.4 eV) [117] from the XPS analysis. The increase in oxygen-containing fractions follows the trend: Pd/CNTs (11.37 at.%) < Pd/N-CNTs (12.72 at.%) < Pd/N-CNTs-1%

**Figure 7** Conversion (a) and selectivity (b) of benzyl alcohol over CNTs, N-CNTs, Pd/CNTs, Pd/N-CNTs and Pd/N-CNTs-1% catalysts.

**Table 7** Catalytic performances of benzyl alcohol oxidation over Pd catalysts

Entry	Catalyst	Pd loaded (wt%)	Time (h)	Conv. (%)	Sel. (%)	TOF (h <sup>-1</sup> )	Refs.
1	Pd-NC-ZS/10t	3	4	64	> 99	–	[104]
2	Pd/MagSBA	3	9	71	83.2	633	[105]
3	Pd/CNTs	1	1	17	91.3	1691	[30]
4	Pd@PBFS-500	1	0.5	87	> 99	690	[106]
5	Pd/N-CNTs	9	3	57	85	–	[35]
6	Pd/AC	1	3	18	91	30	[107]
7	Pd/N-CNTs	5	3	98	38	–	[35]
8	Pd/N-CNTs	5	3	96	96	10560	This work
9	Pd/N-CNTs-1%	5	3	98	> 99	10780	This work

(18.22 at.%). According to the FTIR and XPS results, carboxyl groups on the surface of N-CNTs-OT were capable of interacting with Pd NPs via covalent bonding [95]. Hence, the Pd/N-CNTs-OT catalyst played a critical role in preventing Pd NPs from leaching during the Suzuki coupling reaction and also in the solventfree benzyl alcohol oxidation, and this is due to the available binding sites (i.e. O–C=O, C–N, and C–O–C groups) available in N-CNTs-OT carbon support.

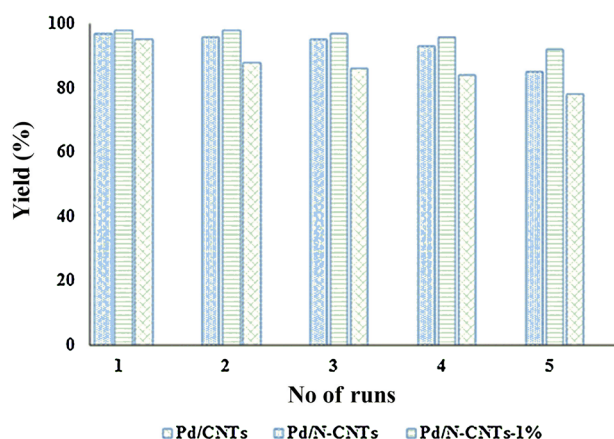
### Catalyst recyclability

The catalytic activities of the three catalysts were studied under the optimized conditions. The recyclability of the catalysts was investigated for iodobenzene and phenylboronic acid as a test substrate by filtration, and the results are illustrated in Fig. 8. The catalysts were washed with ethanol and subsequently with acetone and dichloromethane and dried overnight in an oven at 373 K after each run. The catalytic properties of the three catalysts remained unchanged until after the fifth runs, with no loss in their selectivity and activity. The Pd/CNTs become less active with a drop in yield to 84% after the fourth run, while Pd/N-CNTs and Pd/N-CNTs-1% showed the highest stability with a 93% yield after the fifth run. Further TEM analysis of the catalysts after five runs showed well-dispersed Pd NPs (Supplementary Figure S5) with minimal agglomeration. Table 8 shows the recyclability of the catalyst after seven runs for benzyl alcohol oxidation. The Pd/N-CNTs-1% catalyst produced an outstanding conversion of 96% after seven recycles of reaction regeneration, signifying even Pd NPs dispersion, high stability and robust interaction between carbon

support and Pd NPs, thus preventing not only agglomeration but also leaching.

### Pd leaching test

Leaching of metal NPs is of great concern in heterogeneous catalysis, and to confirm the amount of metal leached, the hot filtration test method was employed to investigate whether the Pd/CNTs and Pd/N-CNTs acted as heterogeneous catalysts. Similar catalyst amounts and reaction conditions for Suzuki reaction were employed for the hot filtration experiment. After 20 min of reaction, the catalyst was filtered, and the filtrate was analysed through ICP-OES. For the reaction, 36% conversion was recorded, and no trace of Pd species was detected. The reaction was allowed to proceed until after 120 min. It was observed that the reaction was halted after catalyst removal, indicating no further conversion (Supplementary Figure S6). We suggested that Pd species from Pd/N-CNTs-1% catalyst remain active in the

**Figure 8** Recyclability of Pd catalysts for Suzuki coupling reactions.

**Table 8** Reusability of the Pd/N-CNTs-1% catalyst for the oxidation of benzyl alcohol

Runs	1	2	3	4	5	6	7
Yields	96	96	96	96	95	95	92

catalytic cycle (i.e. oxidative addition, transmetalation and reductive elimination) of Suzuki reaction (Supplementary Figure S7), thus preventing catalyst loss and permitting easy recovery. The observed stability, catalytic efficiency and reusability of Pd/N-CNTs and Pd/N-CNTs-1% catalyst make them a suitable candidate for C–C coupling reactions and oxidation reactions.

Further ICP-OES analysis was carried out after the fifth run with 4.56 wt% Pd content recorded for Pd/N-CNTs and Pd/N-CNTs-1%, indicating a strong interaction of Pd NPs with the active sites of the carbon support thereby thwarting leaching. A combination of the results of recyclability and the hot filtration test showed that the catalyst is genuinely heterogeneous and selective towards Suzuki coupling and oxidation of benzyl alcohol reactions without significant Pd leaching.

## Conclusion

Pd/CNTs, Pd/N-CNTs and Pd/N-CNTs-1% catalysts were successfully synthesized by MOCVD techniques. Pd NPs sizes of 3.4, 7.3 and 8.7 nm were well dispersed on N-CNTs, N-CNTs-1% and CNTs, respectively. The catalysts possessed mesoporous surfaces with reasonable stability and excellent durability. The correlation of metal–carbon interaction, particle size distribution and the effect of pyrrolic-N atoms towards excellent catalytic activity and selectivity of Pd/N-CNTs-1% was successfully archived for Suzuki coupling and benzyl alcohol oxidation reactions. It must be stressed that 1% weight of oxygen atom, introduced by benzophenone, and seen from XPS result of Pd/N-CNTs-1%, is useful for applications where strong interfacial bonding of Pd NPs with carbon support is required.

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## Compliance with ethical standards

**Conflict of interest** The authors declared that they have no conflict of interest.

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