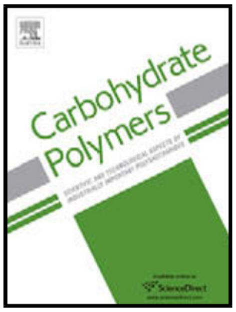

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Combination of carbon nanotube and cyclodextrin nanosponge chemistry to develop a heterogeneous Pd-based catalyst for ligand and copper free C-C coupling reactions

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Highlight

- A novel hybrid system composed of carbon nanotubes and cyclodextrin nanosponge have been prepared and used for immobilization of Pd nanoparticle.
- The synergism between carbon nanotubes and cyclodextrin nanosponge was confirmed.
- A novel procedure for ligand and copper-free Sonogashira and Heck reaction is developed.
- The catalyst was highly recyclable with negligible Pd leaching.

Abstract

Carbon nanotubes and cyclodextrin nanosponge were hybridized and used as a support for embedding Pd(0) nanoparticles and developing a novel and heterogeneous catalyst, Pd@CDNS-CNT, for promoting ligand and copper-free Sonogashira and Heck coupling reactions in aqueous media and mild reaction condition. Cyclodextrin nanosponge could contribute to catalysis through encapsulating the reagents and transferring them in the vicinity of Pd nanoparticles. The results established that the catalytic activity of Pd@CDNS-CNT was superior to those of Pd@CNT, Pd@CDNS and Pd@CNT+CDNS, indicating the synergism between the components of the hybrid system. Notably, various aryl halides including aryl iodide, bromide and chloride were useful substrates for the coupling reactions and affording the corresponding products in high to excellent yields in short reaction times. Moreover, the catalyst was recyclable up to six reaction runs with negligible Pd leaching.

Keywords: Carbon nanotubes, Cyclodextrin nanosponge, Pd nanoparticles, Hybrid catalyst, C-C coupling reactions.

1. Introduction

Recently, the utility of cyclodextrins, CDs, as monomers for preparation of hyper-cross linked polymers, referred as cyclodextrin nanosponges (CDNS), has been disclosed. Using various types of cross-linking agents and CDs, synthetic procedure and the ratio of CDs to cross-linking agents, the crystallinity, morphology and the cavities of CDNS can be tuned (Trotta, 2011; Tejashri, Amrita&Darshana, 2013). The presence of both cavities of CDs and the cavities of 3D polymeric network makes CDNS a proper candidate for accommodating various guest molecules with diverse range of size, shape and polarity (Swaminathan, Pastero, Serpe, Trotta, Vavia, Aquilano, Trotta, Zara&Cavalli, 2010; Trotta, Cavalli, Martina, Biasizzo, Vitillo, Bordiga, Vavia&Ansari, 2011). Besides this feature, CDNS exhibited high thermal and pH stability and biocompatibility (Trotta, 2011; Shende, Deshmukh, Trotta&Caldera, 2013; Torne, Darandale, Vavia, Trotta&Cavalli, 2013; Shringirishi, Prajapati, Mahor, Alok, Yadav&Verma, 2014). Hence, they have been widely used for developing drug delivery systems (Cavalli, Trotta&Tumiatti, 2006; Anandam&Selvamuthukumar, 2014). Moreover, CDNS have attracted growing attention in the field of waste water treatment and catalysis (Arkas, Allabashi, Tsiourvas, Mattausch&Perfle, 2006; Di Nardo, Roggero, Campolongo, Valetti, Trotta&Gilardi, 2009; Boscolo, Trotta&Ghibaudi, 2010; Trotta, 2011; Cintas, Cravotto, Gaudino, Orio&Boffa, 2012; Cravotto, Calcio Gaudino, Tagliapietra, Carnaroglio&Procopio, 2012).

Carbon-based nanomaterials such as graphene sheets, carbon nanotubes, carbon nanofibers, carbon spheres have been widely used as support for development of various photo, electro-catalysts. Among carbon nanomaterials, single and multi-walled carbon nanotubes, CNTs, have been considered as promising supports due to their outstanding properties such as high surface area, electric conductivity, inertness, surface tune-ability through functionalization, and thermal and chemical stability (Ombaka, Ndungu&Nyamori, 2013; Hiltrop, Masa, Maljusch, Xia, Schuhmann&Muhler, 2016; Wang, Chu, Wang, Yang&Jiang, 2016; Fan, Fan, Wang, Xiang, Tanga&Sun, 2017).

Heck and Sonogashira reactions are of Pd catalyzed C-C coupling reactions. The importance of these reactions lies in their utilities for the synthesis of diverse range of complex organic compounds, including natural products and biologically active chemicals (Lin, Huang , Wu, Mou &Tsai 2010). Traditionally, phosphine ligands as well as copper co-catalysts have been employed together with homogeneous Pd catalysts (Chinchilla&Nájera, 2011; Hajipour, Shirdashtzade&Azizi, 2014). Use of homogeneous catalysts can make the recyclability of the catalyst tedious. Hence, development of a heterogeneous Pd catalyst which could promote the C-

C coupling reactions in the absence of co-catalysts and ligands under green and eco-friendly conditions has gained tremendous attention (Gholap, Venkatesan, Pasricha, Daniel, Lahoti&Srinivasan, 2005; Thorwirth, Stolle&Ondruschka, 2010; Bakherad, 2013; Hajipour, Shirdashtzade&Azizi, 2014; Nasrollahzadeh, Khalaj&Ehsani, 2014; Nasrollahzadeh, Maham&Tohidi, 2014; Roya, Mondal, Banerjee, Mondal, Bhaumik&Manirul Islam, 2014; Zhou, Wang, Jiang, Fu, Zheng, Zhang, Chen&Li, 2014; Nasrollahzadeh, Sajadi, Maham&Ehsani, 2015; Shunmughanathan, Puthiaraj&Pitchumani, 2015; Esmaeilpour, Sardarian&Javidi, 2016; Bakherad, Doosti, Mirzaee&Jadidi, 2017; Rathod&Jadhav, 2017). In this line, immobilization of Pd nanoparticles supported on tubular inorganic functionalized materials such as poly(*N*-isopropylacrylamide)-functionalized halloysite nanotubes (Massaro, Schembri, Campisciano, Cavallaro, Lazzara, Milioto, Noto, Parisi&Riela, 2016) as well as organic nanotubes such as CNT (Siamaki, Lin, Woodberry, Connell&Gupton, 2013; Ohtaka, Sansano, Nájera, Miguel-García, Berenguer-Murcia&Cazorla-Amorós, 2015) has been reported.

In continuation of our efforts to develop novel heterogeneous catalysts (Sadjad, Heravi, Zadsirjan&Farzaneh, 2017; Sadjadi, Heravi&Malmir, 2017; Sadjadi, Hosseinnejad, Malmir&Heravi, 2017; Sadjadi, Malmir&Heravi, 2017), recently we focused on the utility of CDNS for embedding catalytic active species (Sadjadi, Heravi&Daraie, 2016; Sadjadi, Heravi&Daraie, 2017). The promising performance of CDNS can be attributed to its capability to encapsulate the catalytic active species as well as substrates within its cavities and bringing them in close contact to the catalytic species. On the other hand, the utility of CNT as catalyst support has been well-established. However, one of the drawbacks of CNT is its insolubility in aqueous media, which can limit its applications. To furnish a solution to this problem and develop a heterogeneous catalyst with high catalytic activity in aqueous media, a novel hybrid system, CDNS-CNT, was designed and used for immobilizing Pd(0) nanoparticles. As CDNS can host the hydrophobic substrates in its cavities and bringing them in the vicinity of the catalytic active sites, it can act as phase transfer agent. The catalytic activity of the catalyst, Pd@CDNS-CNT, for two important C-C coupling reactions, Sonogashira and Heck reactions (Schemes 1 and 2 in supporting information), was investigated. Moreover, the catalyst recyclability and Pd leaching was examined.

2. Experimental

2.1. Materials and Instruments

The catalyst was prepared using multi-walled carbon nanotubes, MWCNTs (provided from US NANO), (3-chloropropyl) trimethoxysilane, *N*-[3-(trimethoxysilyl)propyl] ethylenediamine (AEAPTMS), diphenyl carbonate, β-cyclodextrin, $Pd(OAc)_2$, $NaBH_4$, HNO_3, H_2SO_4, toluene and MeOH. All the chemicals were purchased from Sigma-Aldrich and used without any purification.

The chemicals employed for studying the catalytic activity of Pd@CDNS-CNT included K_2CO_3, acetylenes, aryl halides, alkenes and distilled water. All were provided from Merck and used as received.

Characterization of Pd@CDNS-CNT was performed by using BET, XRD, FTIR, TEM, TGA, SEM/EDS and ICP-AES. N_2-adsorption-desorption isotherm of Pd@CDNS-CNT was recorded by using BELSORP Mini II apparatus. The catalyst and other samples subjected to BET analyses were degassed by pre-heating at 423 K for 3 h. TEM images were obtained by using Philips CM30300Kv field emission transmission electron microscope. To record SEM/EDS images, Tescan instrument, using Au-coated samples and acceleration voltage of 20 kV was applied. Thermo gravimetric analyses (TGA) was carried out by using a METTLER TOLEDO thermo gravimetric analysis instrument with a heating rate of 10°C min^{-1} from 40 to 730°C under N_2 atmosphere. X-ray diffraction pattern of the catalyst was achieved by using a Siemens, D5000. CuKα radiation from a sealed tube. To obtain FTIR spectra of the catalyst and other components, PERKIN-ELMER- Spectrum 65 instrument was used. The ultrasonic apparatus used for the synthesis of Pd@CDNS-CNT was Bandelin HD 3200 with output power of 150 W and tip TT13.

The progress of Sonogashira and C-C coupling reactions was monitored by using thin layer chromatography (TLC) on commercial aluminum-backed plates of silica gel 60 F254, visualized, using ultraviolet light. All the obtained coupling products were known and their formation was confirmed by comparing their melting points, determined in open capillaries using an Electrothermal 9100 without further corrections, and FTIR spectra with authentic samples. Moreover, ^{1}HNMR and ^{13}CNMR spectra of some selected products were recorded by applying Bruker DRX-400 spectrometer at 400 and 100 MHz, respectively.

2.2. Synthesis of CDNS

CDNS, **1**, was prepared through previously reported melting methodology (Cavalli, Trotta&Tumiatti, 2006; Swaminathan, Pastero, Serpe, Trotta, Vavia, Aquilano, Trotta, Zara&Cavalli, 2010; Trotta, Cavalli, Martina, Biasizzo, Vitillo, Bordiga, Vavia&Ansari, 2011). Typically, cross-linking agent, diphenyl carbonate, (8 mmol) was heated at 100°C to melt. Then, the monomer, β-cyclodextrin (1 mmol) was added slowly to the melted diphenyl carbonate. To allow the cross-linking reaction between the two components to proceed, the mixture was stirred at 120 °C for 12 h. Subsequently, the resulting precipitate was cooled to ambient temperature and crushed. Then the product was purified by washing with acetone and distilled water. Further purification was accomplished by Soxhlet extraction with EtOH for 4 h. Finally, CDNS was dried in an oven at 80 °C overnight.

2.3. Amine-functionalization of CDNS: CDNS-N

CDNS (1.2 g) was suspended in dry toluene and homogenized by using ultrasonic irradiation of power 100 W for 15 min. Then, a solution of AEAPTMS (4 mL in 20 mL dry toluene) was added to the homogenized CDNS suspension dropwise and the resulting mixture was refluxed overnight. Upon completion of the reaction, the white precipitate, **2**, was filtered and washed several times with dry toluene and dried at 90 °C overnight.

2.4. Modification of CNTs surface: synthesis of CNT-OH

MWCNTs (1.5 g) was suspended in acidic mixture of H_2SO_4 and HNO_3 (1:1) and refluxed at 55 °C for 24 h. Then, the resulting mixture was diluted 5 times with distilled water to reach the neutral pH. After filtration via centrifuge, the sample was dried in vacuum oven at 50 °C for 24 h. To reduce the acidic and other carbonyl functionalities on the surface of CNT and provide –OH functionalities, the solid was treated with $NaBH_4$ in methanol for 24 h.

2.5. Synthesis of CNTs-Cl :

To introduce Cl functionality on the surface of CNT, CNT-OH (2.1 g) was suspended in xylene (100 mL) and then 3-chloropropyltrimethoxysilane (2.5 mL) was added. The resulting mixture was then refluxed for 24 h. Upon completion of the reaction, the obtained solid was washed with methanol in order to remove the un-reacted residue of organosilane. Finally, CNT-Cl was obtained by drying in vacuum oven at 80 °C overnight.

2.6. Synthesis of CNT-CDNS hybrid

To hybridize CNT-Cl and CDNS-N, CNTs-Cl (2.25 g), CDNS-N (0.75 g) and catalytic amount of ammonia (0.5 mL) were mixed in toluene (100 mL). The resulting mixture was then refluxed for 24 h. CNT-CDNS hybrid was obtained by drying in vacuum oven at 110 °C.

2.7. Immobilization of Pd nanoparticles: Synthesis of Pd@CDNS-CNT

To immobilize palladium nanoparticles, CDNS-CNT (1.2 g) was dispersed in dry toluene (15 mL) and then a solution of $Pd(OAc)_2$ (0.02 g) in MeOH (10 mL) was added dropwise. The resulting mixture was then stirred at room temperature for 8 h. To reduce Pd salt to Pd(0), a solution of $NaBH_4$ in a mixture of toluene and MeOH (10 mL, 0.2 N) was added dropwise into the above-mentioned mixture and the suspension was mixed for 3 h. Finally, Pd@CDNS-CNT was obtained by washing with MeOH and drying in oven at 60 ^{o}C for 12 h, Figure 1 in supporting information.

To prepare Pd@CNT and Pd@CDNS, the similar procedures were used except, CNT-OH and CDNS-N were used as supports.

2.8. Typical procedure for Sonogashira reaction

Pd@CDNS-CNT (25 mg) as catalyst, K_2CO_3 (2.0 mmol) as base, aryl halide (1.0 mmol) and acetylene (1.2 mmol) as reagents were mixed in distilled water and then heated at 50 °C under stirring condition. The progress of the reaction was traced by TLC. At the end of the reaction, Pd@CDNS-CNT was filtered off and the reaction mixture was cooled to ambient temperature. Subsequently, the organic layer was extracted with diethyl ether, purified by column chromatography over silica gel by using-hexane/ethyl acetate (4:1) as eluent to furnish the corresponding coupling product.

2.9. Typical procedure for the Catalytic Mizoroki–Heck Reaction

Arylhalide (1.0 mmol), alkene (1.5 mmol), K_2CO_3 (2 mmol) and Pd@CDNS-CNT (30 mg) were mixed in water (4.0 mL). Then, the obtained mixture was stirred at 100°C for appropriate reaction time. At the end of the reaction (traced by TLC), Pd@CDNS-CNT was filtered, washed with ethanol and dried at 90°C and used for the consecutive reaction run. Then, the organic layer, extracted with diethyl ether, was washed with H_2O, separated and dried over anhydrous Na_2SO_4. Purification was achieved by recrystallization.

3. Result and discussion

3.1. Catalyst characterization

To confirm the formation of CDNS-N, CNT-Cl, CDNS-CNT and Pd@CDNS-CNT, their FTIR spectra were recorded and compared, Figure 1. As depicted, the FTIR spectrum of CDNS-N, Figure 1, showed the characteristic bands of CD, i.e. the bands at 3370 cm^{-1}, 1621 cm^{-1}, as well as a band at 1747 cm^{-1}, which is the characteristic band of (-C=O) and confirm the cross-linking of CDs with diphenyl carbonate. Moreover, the bands at 2926 cm^{-1} and 1030 cm^{-1} can be attributed to the $–CH_2$ and Si–O stretching, indicating the conjugation of AEAPTMS. The FTIR spectrum of CNT-Cl also contains the bands at 1000 cm^{-1} (Si–O stretching) and 2921 cm^{-1}($–CH_2$ stretching), implying the successful attachment of 3-chloropropyltrimethoxysilane on the surface of CNT. The FTIR spectra of both CDNS-CNT and Pd@CDNS-CNT exhibited the characteristic bands of CDNS-N and CNT, confirming the successful formation of hybrid system. Comparing the FTIR spectra of CDNS-CNT and Pd@CDNS-CNT, showed that the intensities of the bands of the latter were slightly lower than those of the former. This can be indicative of Pd nanoparticle incorporation.

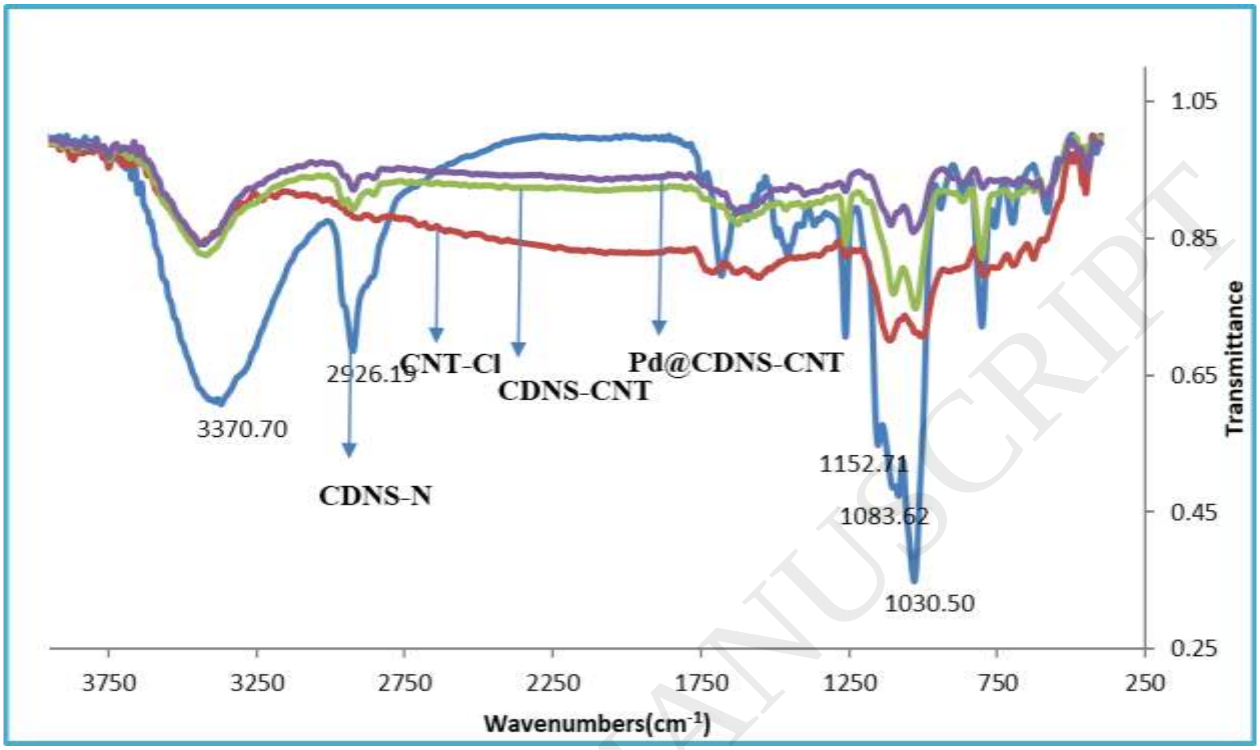


Figure 1. The FTIR spectra of CDNS-N, CNT-Cl, CDNS-CNT, Pd@CDNS-CNT

The XRD patterns of CNT-F, CDNS-CNT and Pd@CDNS-CNT are shown in Figure 2. The XRD pattern of CNT-F exhibited the characteristic peaks at $2\theta = 22°$, 23.4°, 26°, 31°, 34°, 37°, 43°, 46° and 52°. The XRD pattern of CDNS-CNT showed the characteristic bands of CNT-F as well as broad halo $2\theta = 20°$, which can be assigned to CDNS. The XRD pattern of the catalyst is similar to that of CDNS-CNT and no characteristic peaks for Pd(0) nanoparticles was observed. According to the literature, this issue can be due to the low amount of Pd loading (as it was confirmed by ICP-AES analysis) and high distribution and small particle size of Pd nanoparticles (Mallik, Dash, Parida&Mohapatra, 2006).

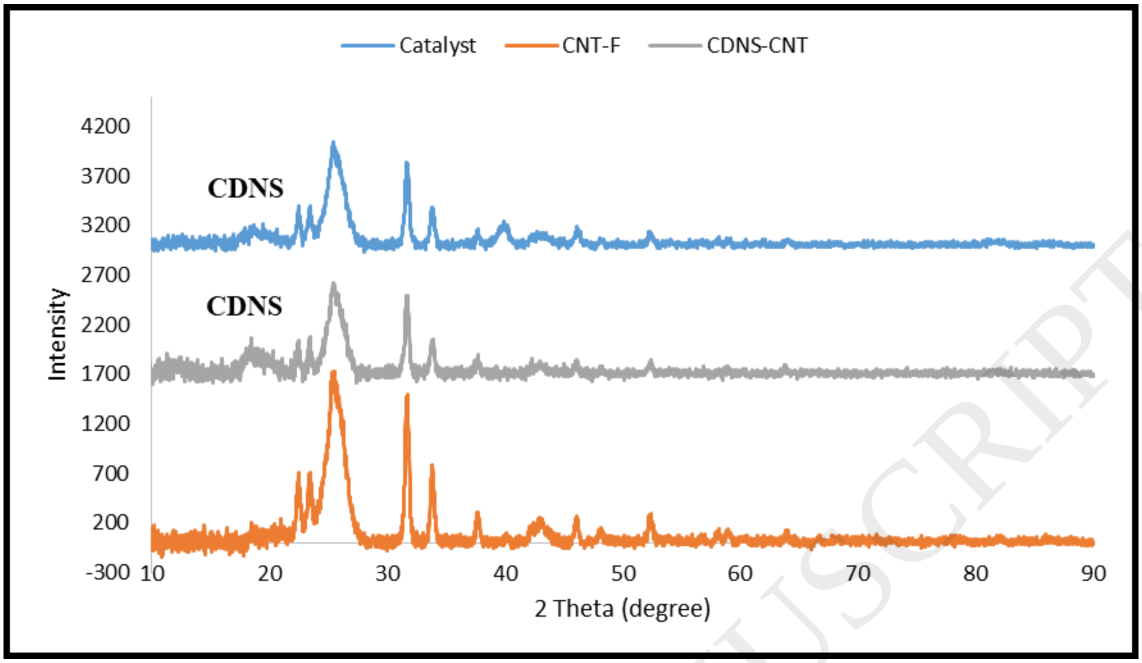
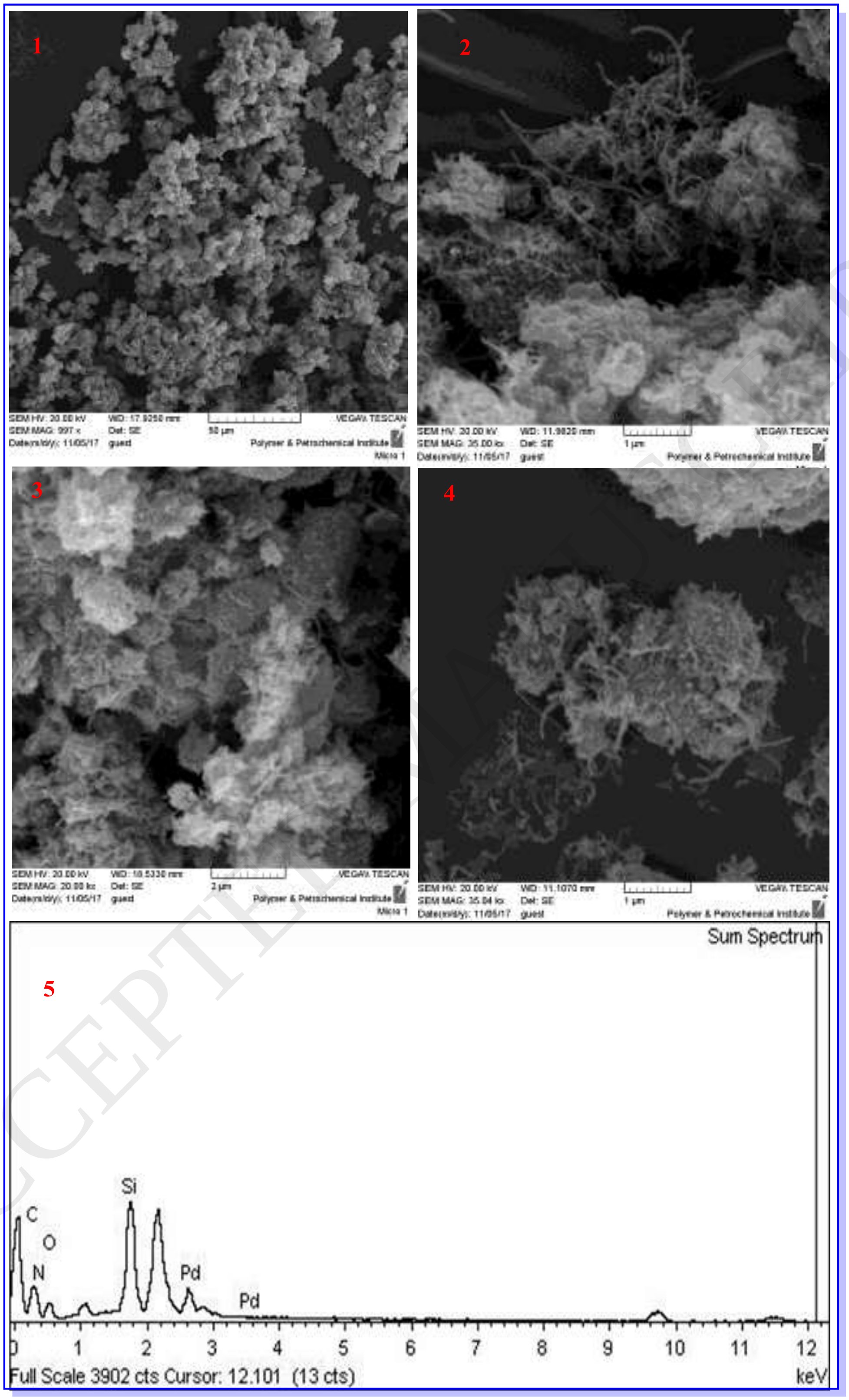


Figure 2. The XRD pattern of CNT-F, CDNS-CNT and Pd@CDNS-CNT

To elucidate the morphology of CDNS-N, CDNS-CNT and Pd@CDNS-CNT and study the effect of hybridization with CDNS and incorporation of Pd, the SEM images of CDNS-N, CDNS-CNT and Pd@CDNS-CNT were recorded and compared, Figure 3. CDNS-N, Figure 3-A-1, exhibited the small particulates packed together to form small aggregates. The morphology of CDNS-CNT hybrid (Figure 3-A-2), however, is totally different. In the hybrid system, the carbon nanotubes are clearly observable and it can be seen that the CNT and CDNS intertwined to form aggregates. Although the SEM images of CDNS-CNT and Pd@CDNS-CNT are almost similar, it can be detected that incorporation of Pd nanoparticles (Figure 4-A3 and 4) can slightly induce more aggregation. In Figure 3-A-5 the EDS analysis of the catalyst is illustrated. As shown, the incorporation of Pd nanoparticles (the presence of Pd atom) can be confirmed. The presence of Si, C, N and O atoms can prove the functionalization of CDNS and CNT with organosilanes. Moreover, the observation of C and O can be attributed to the CDNS component.

Notably, EDS solely was not adequate for confirming the formation the catalyst. Hence, the structure of Pd@CDNS-CNT was confirmed by other analyses.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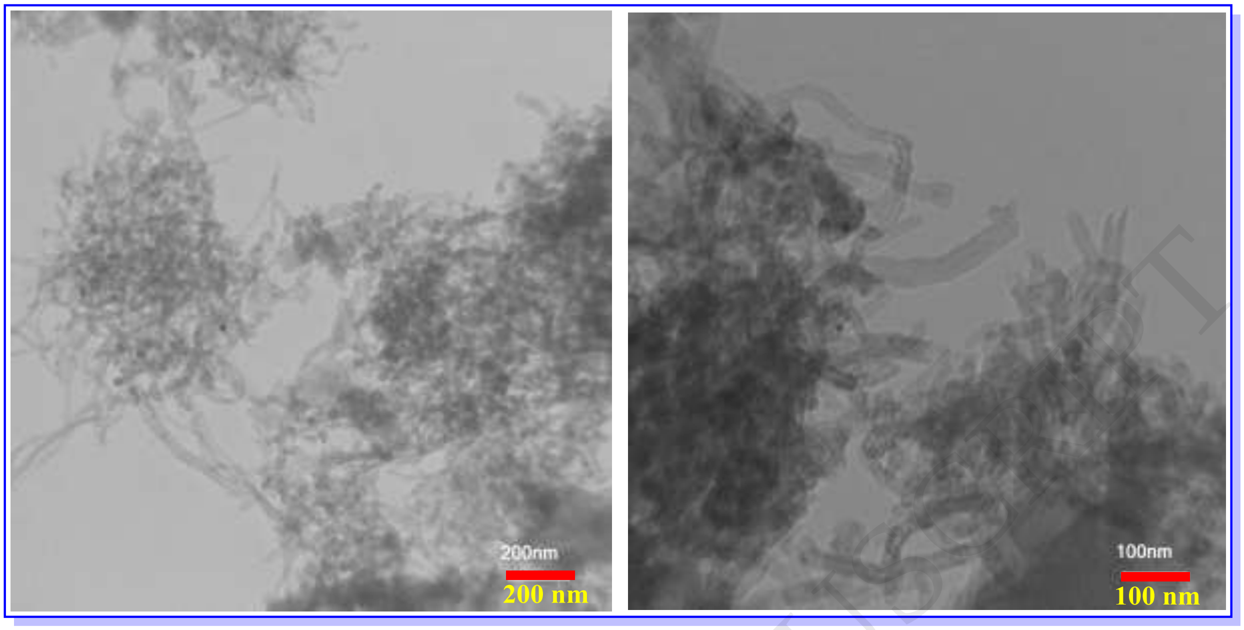

B

Figure 3. A: SEM images of A: CDNS, B: CDNS-CNTC and D: Pd@CDNS-CNT, E: EDS analysis of Pd@CDNS-CNT, B: TEM images of Pd@CDNS-CNT

The morphology of the catalyst was also studied by TEM. The TEM images of Pd@CDNS-CNT are depicted in Figure 3-B. As shown, the carbon nanotubes are covered with CDNS in some parts. Moreover, the black spots can be attributed to the Pd nanoparticles. Using TEM analysis, the average size of Pd nanoparticles were calculated to be ~10 nm.

To measure the amount of Pd nanoparticles on Pd@CDNS-CNT, the catalyst was subjected to ICP-AES analysis. For preparing the sample for analysis, Pd@CDNS-CNT was fully digested in concentrated acidic solution of HCl and HNO_3 and the extract was analyzed by ICP-AES. The result revealed that the content of Pd nanoparticles was about 0.5 w/w %.

In the next step, the catalyst was subjected to the BET analysis. Nitrogen adsorption–desorption isotherm of Pd@CDNS-CNT, Figure 2 in supporting information, corresponds to the type II nitrogen adsorption–desorption isotherm with H3 hysteresis loops (Yuan, Southon, Liu, Green, Hook, Antill&Kepert, 2008), indicating the porous nature of Pd@CDNS-CNT. Notably, the nitrogen adsorption–desorption isotherm of the catalyst is different from that of CDNS, Figure 3 in supporting information.

The BET analyses of Pd@CDNS-CNT and CDNS-CNT established that the specific surface area of CDNS-CNT (32.9 m^2g^{-1}) reduced to 29.2 m^2g^{-1} upon incorporation of Pd nanoparticles. This observation was consistent with the hypothesis that Pd nanoparticles located on the surface of the hybrid system. The average pore diameter of CDNS-CNT exhibited a slight increase upon incorporation of Pd nanoparticles.

Next, thermal stability of Pd@CDNS-CNT was investigated by TGA analysis of Pd@CDNS-CNT, Figure 4. As depicted, the catalyst exhibited several weight losses. The first one occurring below 150 °C, can be attributed to the loss of water molecules. According to the literature (Sadjadi, Heravi&Daraie, 2017), the weight loss observed at about 340 °C can be assigned to the degradation of CDNS. To further confirm this issue and also estimate the weight percent of AEAPTMS, the thermogram of CDNS-N was also obtained, Figure 4. It was shown that CDNS-N exhibited three weight losses in the range of 120-340 °C. The first weight loss can be attributed to the loss of water, the second one can be due to loss of AEAPTMS and the last one can be assigned to the degradation of CDNS. Using this thermogram the content of AEAPTMS was estimated to be about 3 w/w%. It was also confirmed that AEAPTMS degraded before 350 °C.

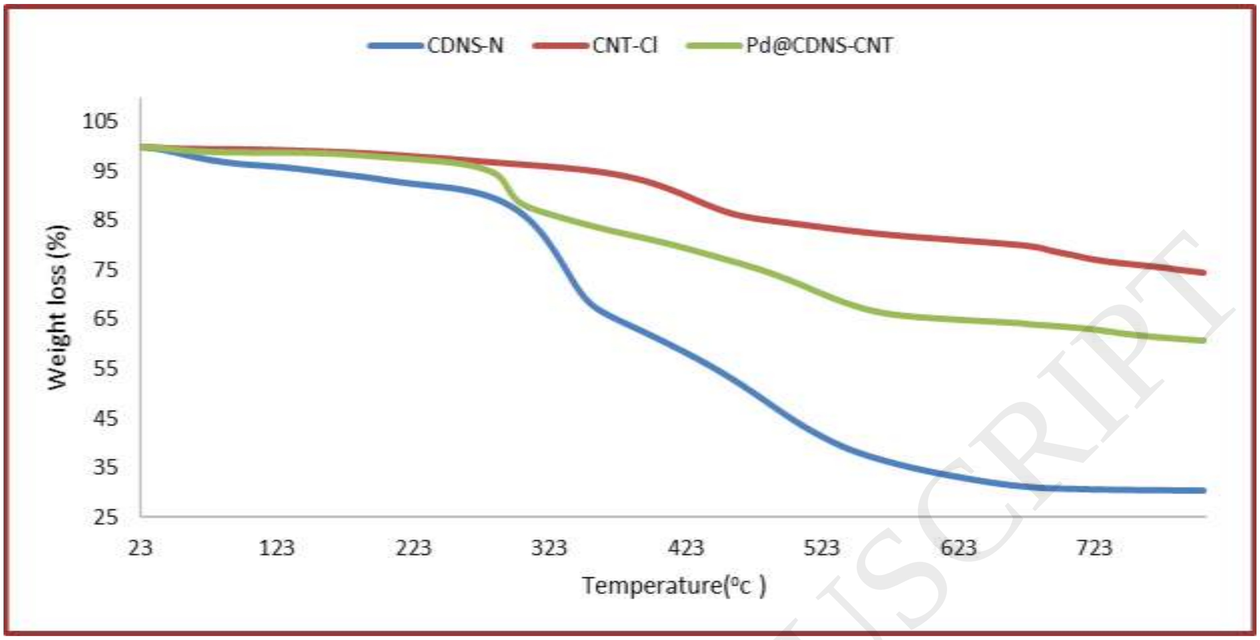

Figure 4. The TGA analyses of CDNS-N, CNT-Cl and Pd@CDNS-CNT

In the thermogram of the catalyst another weight loss was observed at about 370 °C. To elucidate whether it can be attributed to the loss of functionalities on the CNT, the thermogram of CNT-Cl was recorded, Figure 4. Besides loss of water, three more weight losses were observed in the range of 350- 620 °C in the thermogram of CNT-Cl. According to the literature, the weight loss at 620 °C, can be due to the decomposition of CNT (Lehman, Terrones, Mansfield, Hurst&Meunier, 2011). The other losses can be due to the degradation of functionalities on CNT. The percent of these functionalities were estimated to be about 15 w/w%.

The last weight loss in the thermogram of the catalyst was observed at 623 °C. As described above, this can be due to the oxidation of CNT. Using comparing the thermograms, the content of CDNS in the catalyst was calculated to be about 12 w/w%.

3.2. Catalytic activity

The catalytic activity of Pd@CDNS-CNT was examined. Considering the importance of developing an efficient and eco-friendly procedure for C-C coupling reactions, Sonogashira and Heck coupling reactions were targeted as model organic transformations. Initially, the reactions of iodobenzene with acetylene and styrene were selected as model Sonogashira and Heck reactions respectively. The efficiency of Pd@CDNS-CNT for promoting these two model reactions in the absence of copper co-catalyst and ligand in the aqueous media was studied. Gratifyingly, these two reactions could proceed in the presence of catalytic amount of the catalyst and K_2CO_3 to afford the corresponding model products in high yields, Table 1 in supporting information. Motivated by these results, Sonogashira and Heck reactions were optimized by altering the reaction variables, i.e. reaction temperature, catalyst amount, solvent and type of the applied base, and investigating their effects on the yield of desired products, Tables 1 and 2 in supporting information. The results showed that the best solvent and base for both reactions were water and K_2CO_3 respectively. However, the Heck coupling reaction required more amount of the catalyst and elevated reaction temperature compared to Sonogashira reaction. More precisely, Sonogashira reaction could proceed at 50 °C, while the optimum temperature for Heck reaction was 100 °C. Moreover, the optimum amount of the catalyst for Sonogashira and Heck reactions were 25 and 30 mg respectively.

Generality of the developed procedures for Sonogashira and Heck coupling reactions was examined by using various alkenes, alkyenes and aryl halides with electron withdrawing and electron donating groups, Table 3 in supporting information. It was found that all the reagents were useful substrates and afford the corresponding products in high to excellent yields. As expected, in the case of using less reactive aryl chlorides and bromides, lower yields were obtained in longer reaction times compared to aryl iodide. Moreover, reagents with steric hindrance led to lower yields. In the case of Sonogashira coupling reaction, use of aromatic alkenes resulted in higher yields compared to aliphatic ones.

To elucidate whether CDNS can contribute to the catalysis, Pd@CNT was synthesized, see experimental section, and used as a catalyst for promoting the model Sonogashira and Heck coupling reactions. The comparison of the catalytic activity of Pd@CDNS-CNT and Pd@CNT, Table 1, established the superior catalytic activity of the former. This observation confirmed the contribution of CDNS to catalysis. According to the literature (Swaminathan, Pastero, Serpe, Trotta, Vavia, Aquilano, Trotta, Zara&Cavalli, 2010; Trotta, 2011), the role of CDNS in catalysis can be explained based on the potential of CDNS for encapsulation of the substrates in its cavities and bringing them in the vicinity of Pd nanoparticles.

Next, the possibility of the synergistic effect between CDNS and CNT was investigated. Initially, the effect of co-addition of CDNS in the Pd@CNT-catalyzed model Sonogashira and Heck reactions was investigated. More precisely, the model reactions were performed in the presence of Pd@CNT and a catalytic amount of CDNS (Pd@CDNS+CNT), Table 1. The result showed that in the case of use of Pd@CNT, co-addition of CDNS can improve the yield of the products. However, the comparison of the effect of co-addition of CDNS and its inclusion in a single composite on the catalytic activity, i.e. comparison of the catalytic activity of Pd@CDNS+CNT with Pd@CDNS-CNT, established the superior catalytic activity of the latter. This observation indicates the synergistic effects between two components.

In the following, the catalytic activity of Pd@CDNS was investigated and compared with those of Pd@CNT and Pd@CDNS-CNT, Table 1. It was found that the catalytic activity of these catalysts increased in the following order: Pd@CDNS-CNT> Pd@CNT> Pd@CDNS.

Finally, to compare the efficiency of Pd@CDNS-CNT for promoting coupling reactions with those of previously reported catalysts, the yields of the model Sonogashira and Heck reactions under Pd@CDNS-CNT catalysis and previously described condition was compared with some of catalysts and conditions reported in the literature, Table 4 in supporting information. It was found that using Pd@CDNS-CNT as catalysts comparative or higher yields of the products could be achieved in shorter or comparative reaction time with no need to toxic or harmful co-catalyst, ligand, or base.

Table 1. Comparison of catalytic activity of the present catalyst with Pd@CNT and Pd@CNT+CDNS in the Sonogashira coupling reaction of iodobenzene and phenyl and Heck coupling reaction of iodobenzene and methyl acrylate

Entry	Catalyst	Reaction conditions	Yield (%)	Time (h)	[Ref]
		Sonogashira reaction			
1	Pd@CDNS	H_2O/ K_2CO_3/ 50 °C	86	2	This work
2	Pd@CNT	H_2O/ K_2CO_3/ 50 °C	88	1.40	This work
3	Pd@CNT+CDNS	H_2O/ K_2CO_3/ 50 °C	90	1.30	This work
4	Pd@CDNS-CNT	H_2O/ K_2CO_3/ 50 °C	93	1.20	This work
		Heck reaction			
5	Pd@CDNS	H_2O/ K_2CO_3/ 100 °C	85	2.50	This work
6	Pd@CNT	H_2O/ K_2CO_3/ 100 °C	88	2.40	This work
7	Pd@CNT+CDNS	H_2O/ K_2CO_3/ 100 °C	92	2.25	This work
8	Pd@ CDNS-CNT	H_2O/ K_2CO_3/ 100 °C	94	2.10	This work

3.3. Catalyst recyclability

In the following, the recyclability of Pd@CDNS-CNT was investigated. To this purpose, the yields of the model Sonogashira and Heck products, catalyzed by fresh Pd@CDNS-CNT, were compared with the yields obtained through using recycled catalysts. More precisely, upon completion of the first reaction run, the catalyst was recovered by simple filtration and then washed, dried, see experimental section, and subjected to the next reaction run. This recycling was performed up to six reaction cycles, Figure 5, and the yields of the model products were compared. The results established that the catalyst could be successfully recycled for six consecutive reaction runs with only 10% loss of the catalytic activity.

To investigate the effect of recycling of the catalyst on the Pd leaching, Pd content after each reaction run was measured, Figure 5. The results established that this value up to third recycling was negligible. Upon recycling for forth to sixth runs, slight Pd leaching was detected.

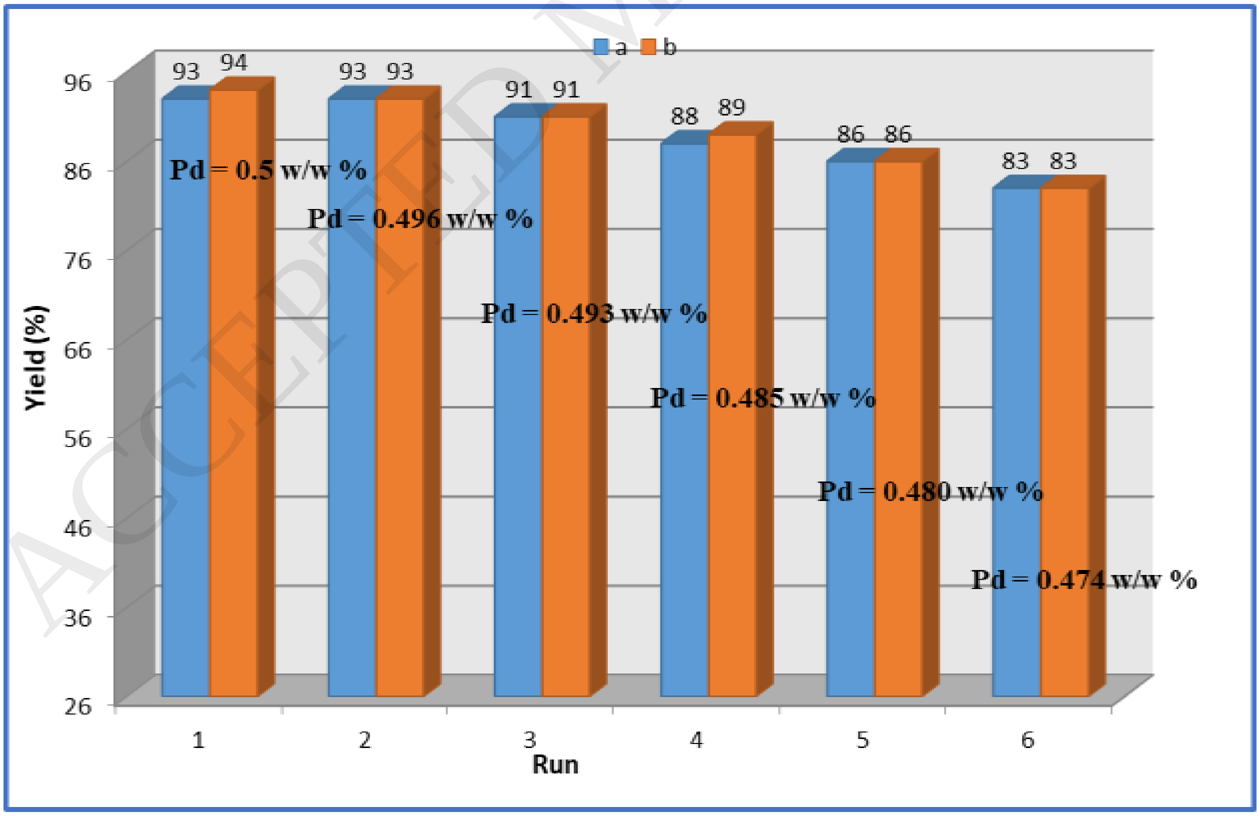

Figure 5. The yields Sonogashira model reaction (a) and Heck model reaction (b) upon recycling of the catalyst and the Pd content in the catalyst in each consecutive reaction run.

To elucidate the stability of Pd@CDNS-CNT upon recovery and recycling, the FTIR spectra of fresh and recycled Pd@CDNS-CNT were recorded and compared, Figure 4 in supporting information. The comparison of two spectra can clearly confirm their similarity, indicating that Pd@CDNS-CNT preserved its structure upon recycling and did not collapse or destruct through recycling.

Finally, to elucidate the effect of recycling on the morphology of Pd@CDNS-CNT, the SEM and TEM images of recycled catalyst was recorded, Figure 6, and compared with those of fresh Pd@CDNS-CNT. As depicted, the SEM images of both fresh and recycled catalysts are similar. The comparison of TEM images also showed the similarity of the morphologies of both fresh and recycled catalysts. However, a slight aggregation was observed. Hence, the slight decrease in the catalytic activity up to six reaction runs can be attributed to both slight Pd leaching and aggregation of Pd nanoparticles upon recycling.

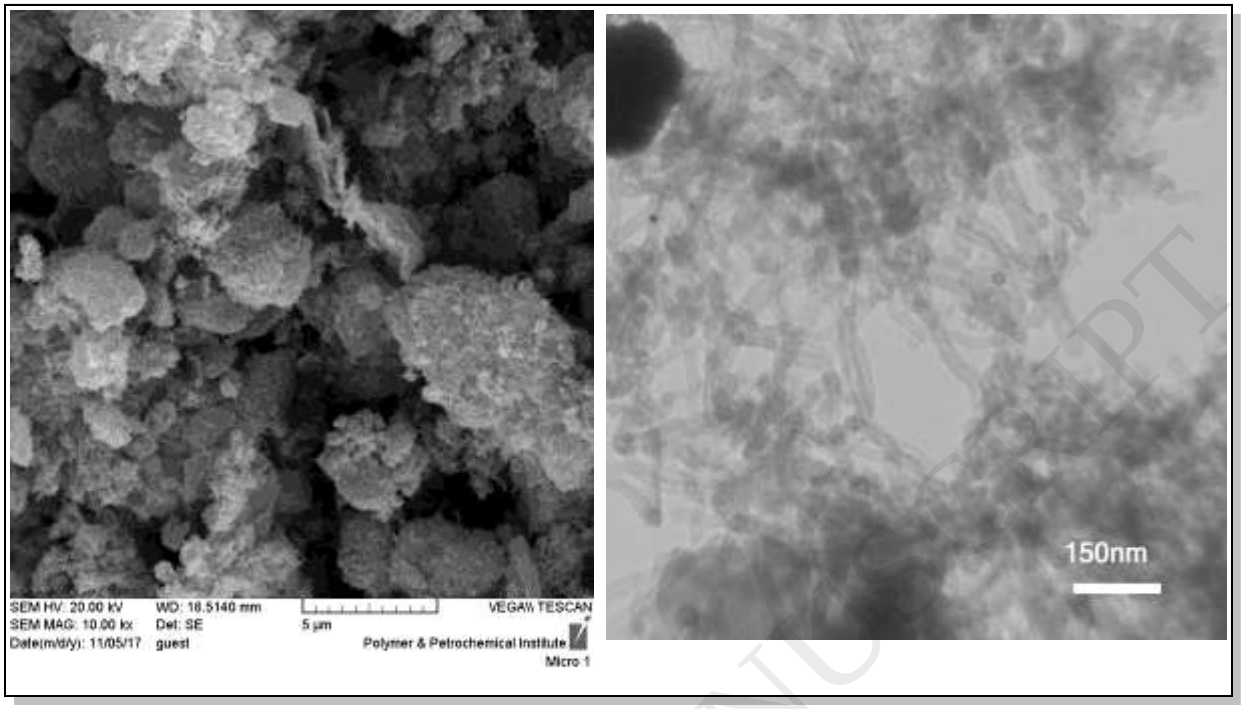

Figure 6. SEM and TEM images of the recycled catalyst.

Conclusion

Combining the capability for CDNS to form inclusion complex with substrate and the outstanding features of CNT as catalyst support, a novel hybrid system, CDNS-CNT, was designed and prepared through reaction of CDNS-N and CNT-Cl. The resulting CDNS-CNT was applied as a support for immobilization of Pd(0) nanoparticles. The obtained catalyst, Pd@CDNS-CNT, was characterized and used for promoting Heck and Sonogashira coupling reactions in aqueous media.

The contribution of CDNS in catalysis was through accommodation of the organic reagent into its hydrophobic cavities and bringing them in the vicinity of the catalytic active sites. On the other hand, the hydrophilic nature of the CDNS, which stems from the presence of hydroxyl groups on the surface of CDs monomers, can allow the reaction proceed in aqueous media. Moreover, comparison of the catalytic activities of the catalyst with those of the control samples, i.e. Pd@CDNS, Pd@CNT and Pd@CNT+CDNS confirmed the superior catalytic activity of the catalyst, indicating the synergism between CDNS and CNT. Notably, Pd@CDNS-CNT exhibited high recyclability (up to six reaction runs) with low Pd leaching and loss of the catalytic activity. The cauterization of the reused catalyst showed that the catalyst was stable upon recycling. However, recycling could cause slight aggregation.

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