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Pd immobilized on polymeric network containing imidazolium salt, cyclodextrin and carbon nanotubes: efficient and recyclable catalyst for the hydrogenation of nitroarenes in aqueous media

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Abstract

A novel polymeric network benefiting from the chemistry of imidazolium salt (IL), cyclodextrin (CD) and carbon nanotube (CNT) is fabricated through a multi-step process, in which silica coated CNTs were vinyl functionalized and polymerized with poly (ethylene glycol) dimethacrylate and CD-IL, prepared from the reaction of vinyl imidazole and tosylated CD. The resulting hybrid system, CNT-P, was then used as a support for the immobilization of Pd nanoparticles and furnishing a heterogeneous catalyst, Pd@CNT-P, with the utility for the hydrogenation of nitroarenes in aqueous media. The catalyst exhibited high catalytic activity and selectivity towards hydrogenation of nitro group. Moreover, it was recyclable up to six reaction runs. Comparing the catalytic activity of the catalyst with that of some control catalysts, the contribution of CD-IL and silica coated CNT to the catalysis has been confirmed. It was believed that CD in the backbone of the catalyst could act as a phase transfer agent, while multiple functional groups on the polymeric moiety improved Pd anchoring and suppressed its leaching. Silica coated CNT on the other hand, allowed better dispersion of Pd nanoparticles and assured fine Pd particle size.

Keywords: Functional polymer, Carbon nanotubes, Cyclodextrin, imidazolium salt, Catalysts, Hydrogenation.

1. Introduction

Polymers are one of the most studied class of supports that have been widely used for the immobilization of various types of catalysts and furnishing heterogeneous catalysts [1, 2]. In this regard, use of polymeric networks that contain functional groups is of great importance [3, 4]. The presence of functional groups can tune the hydrophobicity of the final catalyst. Moreover, the functionalities can act as anchors to effectively stabilize the catalytic species through non-covalent interactions.

Since the discovery of carbon nanotubes, CNTs, their utility in the field of catalysis witnessed tremendous growth. Although CNTs benefit from unique properties such as electric conductivity, thermal and chemical stability, high surface area and inert nature, their low wet ability limited their use in the aqueous media [5-8]. To circumvent this issue, they can be functionalized with hydrophilic components such as polysaccharides and functional polymers [9].

Cyclodextrin chemistry is widely used for the catalytic purposes [10-22]. This cone shape polysaccharide has a unique shape and chemical properties that allow it to act as a phase transfer agent. In more detail, the hydrophobic interior space of CD can readily host the hydrophobic reagents, while the abundant heteroatoms on the surface of CD render it hydrophilic. CD can be applied in its free form as homogeneous catalyst or incorporated in composites or hybrids to develop heterogeneous catalysts [23].

Ionic liquids, ILs, belong to the class of organic salts, in which the cations are mostly heterocycles such as pyridinium and imidazolium, while the anion can be conventional small

anions such as halogens or more complicated anions such as tetrafluoroborate and hexafluorophosphate [24]. ILs possess outstanding properties including, high electric conductivity, low toxicity and melting point. On the other hands, their features can be easily adjusted by altering the entity of the anion and cations [25, 26]. ILs attracted growing attention as catalysts, reaction media and carbon precursors.

Hydrogenation reaction is one of the most important chemical transformation that can be applied for the synthesis of key chemicals in drug and chemical industries. Hydrogenation reactions mostly proceed in the presence of metallic catalysts such as Ru, Rh, Pt and Pd. Despite the efficiency of these metallic catalysts, their scarcity and high costs hinder their widespread applications. To conquer this limitation, use of protocols that require lower content of precious metals as well as heterogenizing the metallic species on a suitable support have been proposed [27-31].

In the continuation of our investigation on the design of heterogeneous catalyst [32-34], recently we disclosed the utility of the hybrids of functionalized polymeric networks for the catalysis [35, 36]. The promising catalytic activity of those systems motivated us to design a polymeric network that benefits from the chemistry of CNT, CD and IL. To prepare the polymer, CNT was first coated with silica layer and then vinyl functionalized. Meanwhile, tosylated CD was prepared and reacted with vinyl imidazole to furnish CD-IL. The polymerization of the later with the functionalized silica coated CNT and poly (ethylene glycol) dimethacrylate (PEGDMA) led to the formation of a functional polymeric network, CNT-P that contained CDs, CNTs and ILs moieties in its backbone. CNT-P was then applied as a support for the immobilization of Pd nanoparticles to afford Pd@CNT-P that could catalyze hydrogenation reaction of nitroarenes in the aqueous media. The selectivity and

recyclability of the catalyst were studied. Moreover, the roles of CD-IL and silica coated CNT in the catalysis were investigated.

2. Experimental section

2.1. Materials

The chemicals used for the preparation of the catalyst included 3-(trimethoxysilane) propyl methacrylate, poly (ethylene glycol) dimethacrylate (PEGDMA), cetyltrimethyl ammonium bromide (CTAB), tetraethyl orthosilicate (TEOS), azobisisobutyronitrile (AIBN), vinyl imidazole, β -CD, Pd(OAc)₂, DMF, toluene, sodium hydroxide, NaBH₄, EtOH and MeOH. All chemicals were of analytical grade and provided from Sigma-Aldrich. Multi-wall carbon nanotubes (MWCNTs) with purity of > 95%, inner diameter of 5-10 nm and outer diameter of 10-20 nm were provided from US Research Nanomaterials.

2.2. Instrument

The formation of the hybrid catalyst was verified by various characterization techniques, including TGA, XRD, FTIR, BET, TEM, and ICP-AES. The XRD pattern of the catalyst was recorded using a Siemens, D5000. Cu K α radiation from a sealed tube. The specific surface area of the catalyst was measured using BELSORP Mini II instrument. For this analysis, the catalyst was pre-heated at 100 °C for 2 h. Recording of FTIR spectra was carried out using PERKIN-ELMER Spectrum 65 instrument. Thermal stability of the catalyst was investigated by applying METTLER TOLEDO thermogravimetric analysis apparatus. To record the catalyst thermogram, inert atmosphere and heating rate of 10 °C min⁻¹ were applied. Pd loading of the catalyst was estimated using ICP analyzer (Varian, Vista-pro). Transmission electron microscope (TEM) images of the catalyst were recorded with a CM30300Kv field emission transmission electron microscope.

2.3. Synthesis of the catalyst

2.3.1. Synthesis of CNT-SiO₂

Coating of CNT with silica was carried out according to the previous report [37]. Briefly, CNT (0.2 g) and CTAB (1.7 g) were dispersed in distilled water to obtain a homogeneous solution under ultrasonic irradiation. Then, NaOH (0.08 g) was added into the aforementioned solution. The resulting mixture was stirred for 30 min at 60 °C. Subsequently, the Solution of TEOS (10 mL) in ethanol was added and the obtained mixture was stirred 24 h at 60 °C. Finally, the product was filtered, washed several times with warm ethanol and dried in oven to furnish 2 g CNT-SiO₂.

2.3.2. Functionalization of CNT-SiO₂: synthesis of CNT-A

To prepare CNT-A, CNT-SiO₂ (2 g) in 30 mL of toluene was subjected to ultrasonic irradiation for 20 min. Then, 1.5 mL of 3- (trimethoxysilane) propyl methacrylate was added to CNT-SiO₂ suspension and the resulting mixture was refluxed at 110 °C for 24 h. Finally, the precipitate was washed several times with toluene and dried at 80 °C oven for 24 hours to afford 2.3 g CNT-A.

2.3.3. Synthesis of cyclodextrin decorated imidazolium salt: CD-IL

First, CD was tosylated with *p*-TsCl through a known procedure [38]. Briefly, to the dissolved CD (15.86 mmol) in pyridine (200 mL), *p*-TsCl (7.9 mmol) was added and the resulting mixture was kept in the refrigerator at 0 °C for 48 h. Subsequently, water (70 mL) was added. An oily product was obtained after solvent evaporation. In the final stage, cold water was introduced to the oily product to furnish a white solid precipitate. The pure CD-OTs was then achieved through recrystallization from water. The yield of the reaction was 24%.

To prepare CD-IL, CD-OTs (3 g) was homogenized in 30 mL of DMF under ultrasonic irradiation. Subsequently, a solution of vinyl imidazole (1.9 g) in DMF (5 mL) was introduced. After stirring under inert atmosphere at 90 °C for 24 h, 20 mL acetone was added into the aforementioned suspension to furnish a white precipitate. The latter was then filtered, washed with acetone and dried at 60 °C overnight to afford 3.3 g CD-IL.

2.3.4. Polymerization of CD-IL, PEGDMA and modified CNT-A: synthesis of CNT-P

CNT-A (1.5 g) with CD-IL (1.5 g) were dispersed in 30 mL of DMF under ultrasonic irradiation of power 100 W for 10 min. Subsequently, the resulting mixture was stirred for 20 min under Ar atmosphere at 70 °C. Then a solution of AIBN (0.3 g) in DMF was added as an initiator and the mixture was stirred for 45 min. In the following, PEGDMA monomer (1.5 mL) was added and the resulting mixture was stirred overnight at 70 °C. Finally, the precipitate was filtered and washed with DMF, MeOH and acetone several times and dried in oven for 12 h to afford 2.5 g product.

2.3.5. Synthesis of Pd@CNT-P

To immobilize Pd nanoparticles on CNT-P, CNT-P (1g) was sonicated in 30 mL of toluene. Then, a solution of 0.02 g of palladium(II) acetate in toluene (10 mL) was added to the aforementioned suspension and the mixture was stirred for 1 h at room temperature. After that, to reduce Pd (II) to Pd (0), a solution of NaBH₄ (75 mg) in MeOH (20 mL) was slowly added into the suspension under Ar atmosphere and the obtained mixture was stirred for an additional 1 h. Finally, the dark precipitate was filtered, washed with methanol and toluene and dried at 70 °C to afford 0.78 g catalyst. The procedure for the synthesis of Pd@CNT-P is depicted in Figure 1.

To measure the content of Pd on the Pd@CNT-P, the known amount of Pd@CNT-P (0.02 g) was digested in 10 mL strong acidic solution prepared by mixing HNO₃ and HCl with volume ratio of 1:1 and then subjected to ICP analysis. The ICP result showed that the loading of Pd in the catalyst was very low (0.21 mmol g⁻¹).

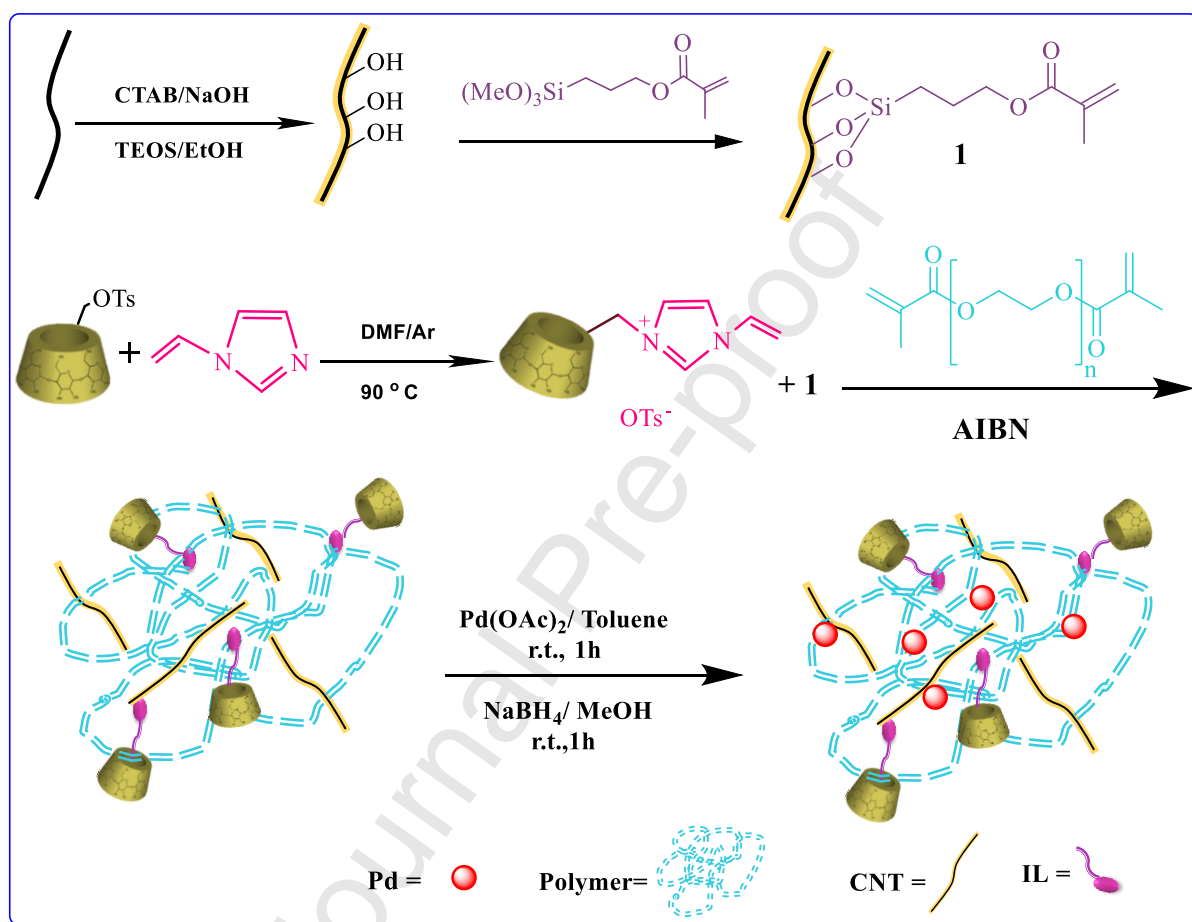


Figure 1. The schematic representation of preparation of Pd@CNT-P.

2.4. Hydrogenation of nitro compounds

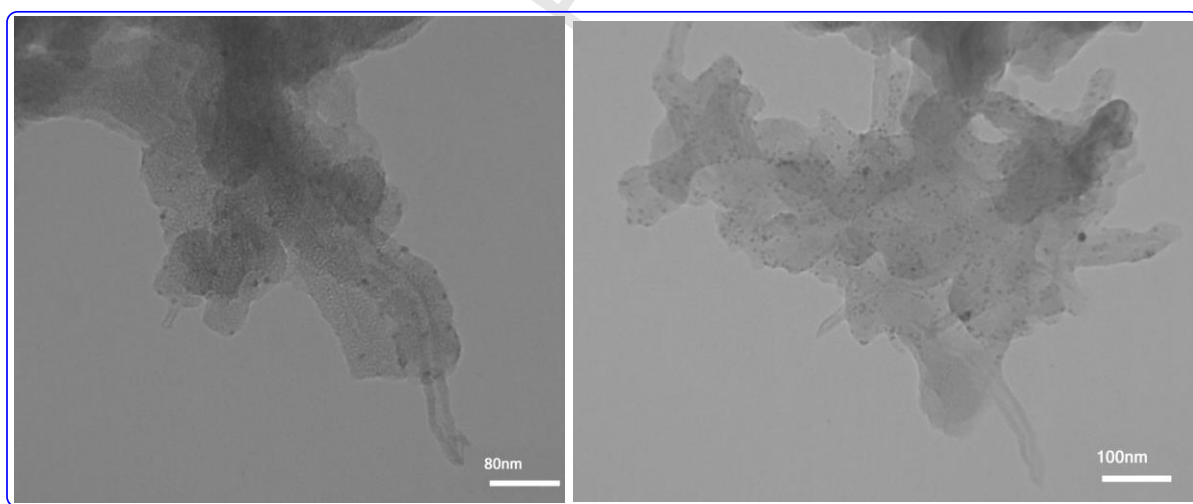
A mixture of nitrobenzene compounds (1 mmol) and Pd@CNT-P (3 wt %) in water as solvent was heated up to 60 °C under H₂ atmosphere (1 bar). Then, the reaction was monitored by thin layer chromatography. Upon completion of the reaction, Pd@CNT-P was separated and

washed several times with ethanol and dried at 90 °C overnight. The final organic amines was achieved via column chromatography.

3. Result and discussion

3.1. Catalyst formation verification

First, to investigate the morphology of Pd@CNT-P, the TEM images of the catalyst were recorded. Two of the TEM images of the catalyst are shown in Figure 2. As depicted, SiO₂-covered CNTs can be detected in the TEM images. Moreover, the polymeric network is observed as a fine sheet. The tiny black dots, on the other hand, can be assigned to the Pd nanoparticles. As can be seen in the histogram of the catalyst, the average particle size of Pd nanoparticles was 2.54±0.97 nm. As shown in the TEM image, these fine Pd nanoparticles were distributed on the CNT-P homogeneously and no aggregation was observed.



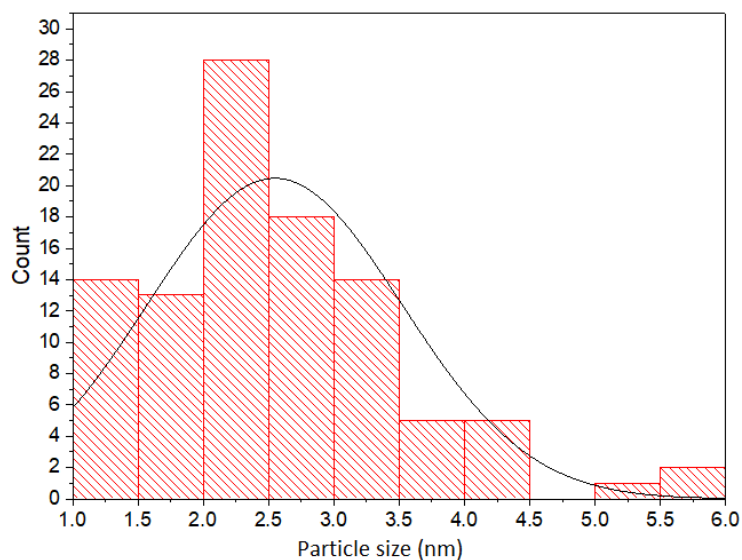


Figure 2. TEM images of the catalyst and the histogram for average Pd particle size.

In the XRD pattern of Pd@CNT-P, Figure 3, the CNT characteristic bands can be detected at $2\theta = 25.1^\circ$, 43.1° and 54° [39]. According to the literature [9], the polymeric network formed from polymerization of PEGDMA, CNT-A and CD-IL is amorphous and its representative band ($2\theta = 15-25^\circ$) overlapped with the band of CNT. Notably, the characteristic bands of Pd nanoparticles cannot be detected in the XRD pattern of the catalyst. This issue can be due to the low loading of Pd as well as their high dispersion [40].

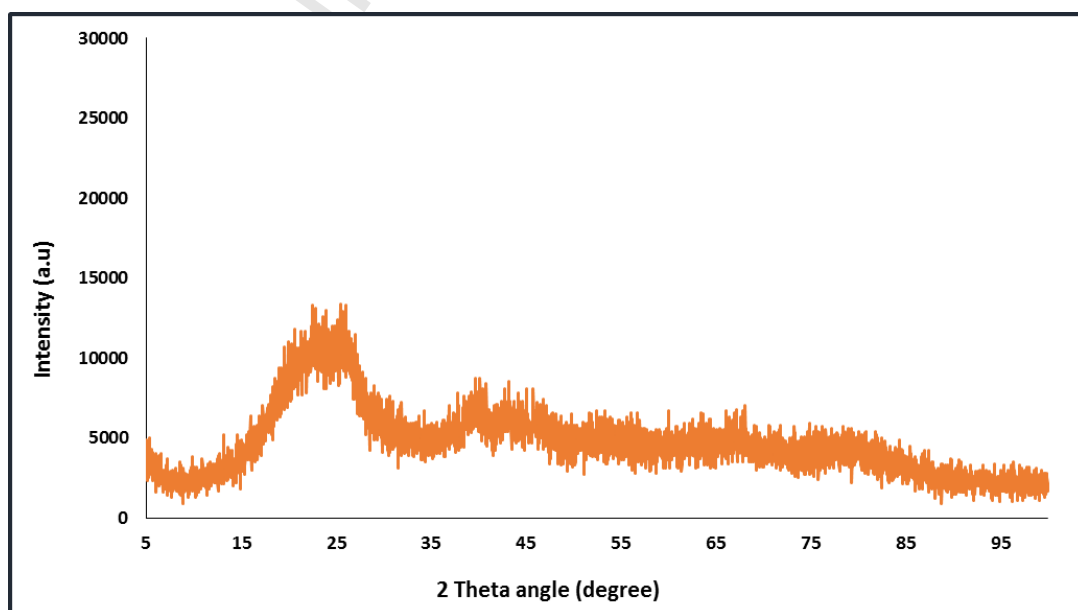


Figure 3. XRD pattern of the catalyst.

In the following, the catalyst was characterized via FTIR spectroscopy. In Figure 4, the FTIR spectrum of the catalyst is presented and compared with that of CNT-SiO₂ and CD-IL. The characteristic bands of CNT-SiO₂ are appeared at 3446 cm⁻¹ (-OH), 2911 cm⁻¹ (-CH₂ stretching) and 1103 cm⁻¹ (Si-O-Si). The FTIR spectrum of CD-IL showed the bands at 3406 cm⁻¹ (-OH) and 2925 cm⁻¹ (-CH₂ stretching) that are related to CD and a band at 1660 cm⁻¹ that can be assigned to -C=N functionality in IL backbone. In the FTIR spectrum of the catalyst, the characteristic bands of CNT and CD-IL can be detected. Moreover, an additional band at 1725 cm⁻¹ can be observed that is representative of -C=O functional groups on PEGDMA and 3-(trimethoxysilane) propyl methacrylate.

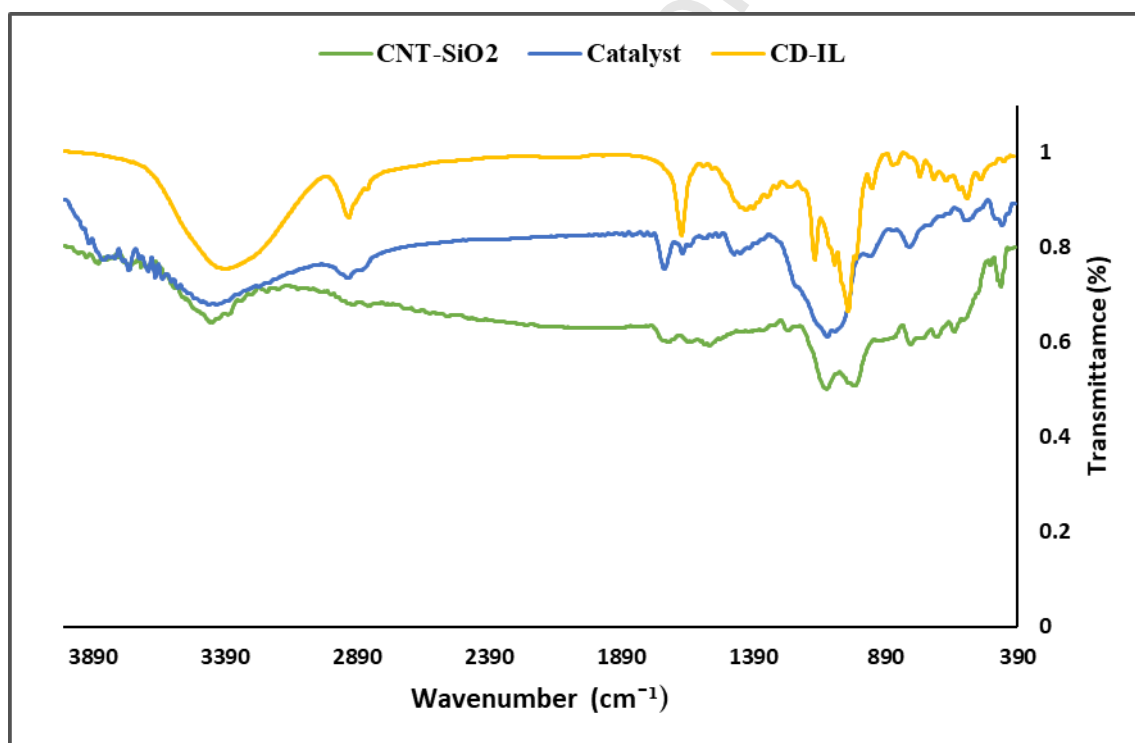


Figure 4. FTIR spectra of Pd@CNT-P, CNT-SiO₂ and CD-IL.

Next, the thermogram of Pd@CNT-P was recorded and compared with that of CD, CD-IL and CNT, Figure 5. The comparison of the thermograms of CD and CD-IL confirmed that the thermal stability of CD-IL is lower compared to that of CD. In detail, CD showed two weight

losses due to the loss of water and the degradation of CD, while in CD-IL, the degradation of IL can also be observed. As shown, the thermal stability of the catalyst is higher than that of CD-IL but lower than that of CNT. This observation can confirm that in the structure of Pd@CNT-P apart from CNT that is a very stable carbon nanostructure, another less thermally stable component (P) is present. Using the TGA, the content of P was estimated to be ~ 50 wt%.

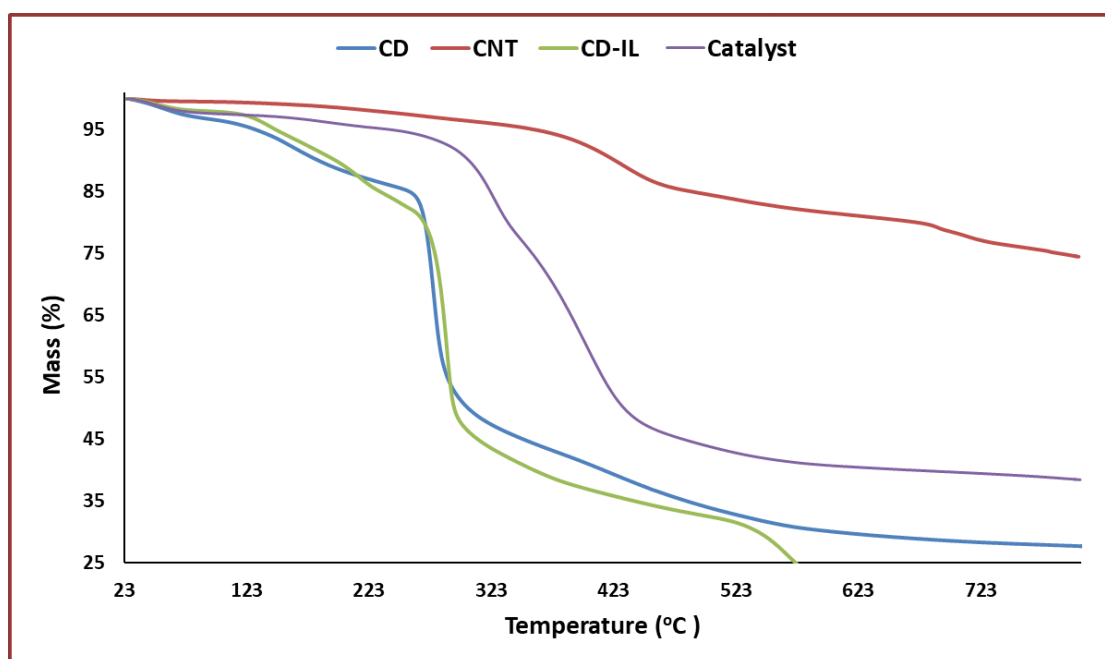


Figure 5. Thermogram of CNT, CD, CD-IL and Pd@CNT-P

The specific surface area of the catalyst, calculated by BET, was measured to be $61.28 \text{ m}^2\text{g}^{-1}$. Nitrogen adsorption–desorption isotherm of the catalyst, shown in Figure 6, was also found to be of type II that is similar to that of CNT.

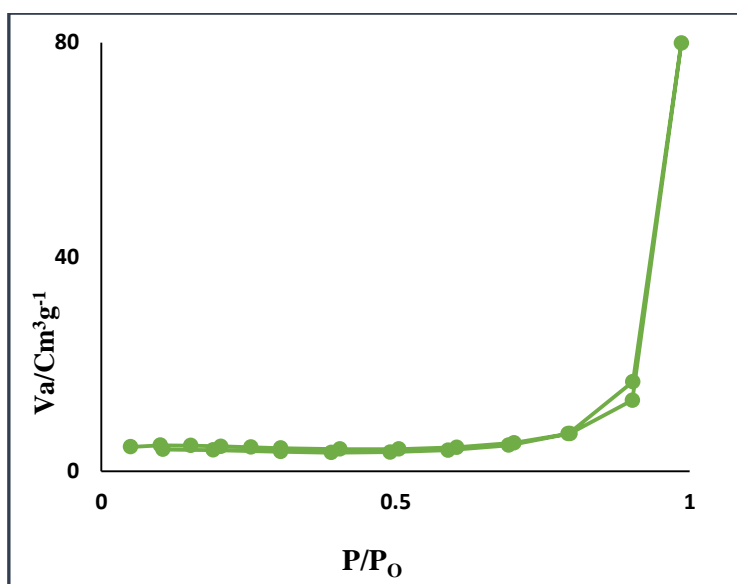


Figure 6. Nitrogen adsorption–desorption isotherm of Pd@CNT-P

3.2. Investigation of the catalytic activity of Pd@CNT-P

After characterization of Pd@CNT-P, its catalytic activity as a heterogeneous catalyst was examined. To initiate the investigation of the catalytic activity, hydrogenation of nitrobenzene as a model hydrogenation reaction was targeted. First, the reaction condition was optimized for the model reaction via examining the effects of various solvents, reaction temperatures and catalyst loadings, Table S1. Initially, the hydrogenation reaction was performed in the presence of 3 wt% of the catalyst in water as an environmentally benign solvent at ambient temperature. It was found that the reaction led to 92% aniline. To improve the reaction yield, the reaction temperature was elevated to 60 °C. Gratifyingly, the yield of the reaction reached to 100% after 2h. Notably, increase of the reaction temperature to 100 °C led to the decrease of the reaction yield. To investigate the effect of the solvent, the reaction was performed in water, EtOH, THF and CH₃CN. The results confirmed that water was the solvent of the choice. Finally, the effect of the catalyst amount was studied by performing the model reaction using 2, 3 and 5 wt% of the catalyst. The results showed that use of 2 wt% of the catalyst resulted in 90% yield of the aniline, while use of 5 wt% of the catalyst affected

neither the reaction yield nor the reaction time. Considering all of these results, the optimum reaction condition was use of water as solvent at 60 °C in the presence of 3 wt% of the catalyst.

Encouraged by the high catalytic activity of the catalyst, the selectivity of Pd@CNT-P was studied by hydrogenation of 4-nitroacetophenone. The result, Table 1, confirmed that the catalyst was 100% selective towards hydrogenation of nitro groups and even in the presence of a competing group, the sole product was 4-aminoacetophenone. In the following, it was investigated whether Pd@CNT-P could hydrogenize steric substrates such as 1-nitronaphthalene. Interestingly, the results, Table 1, confirmed that even substrates with steric hindrance, 1-nitronaphthalene, could tolerate the reaction to furnish 1-aminonaphthalene in high yield. Notably, the reaction of steric substrate required more reaction time and led to lower yield of the product (1-aminonaphthalene) compared to the nitrobenzene. This observation can be attributed to the larger size of 1-nitronaphthalene that makes its encapsulation into CD cavity more tedious compared to nitrobenzene.

Table 1. Hydrogenation of nitro compounds by using Pd@CNT-P^a

Entry	Substrate	Time (h)	Conversion (%)	Yield ^b (%)
1	Nitrobenzene	2	100	100
2	1-Nitronaphthalene	2	100	100
3	4-Nitroacetophenone	3	95	95

^a Reaction conditions: Substrate (1 mmol), catalyst (3 wt %), H₂O (5 mL)

b: Isolated yield.

In the following, the efficiency of Pd@CNT-P for promoting the hydrogenation of nitrobenzene as the model reagent was compared with some of the catalysts that have been previously developed and reported for the same reaction under different reaction condition, Table 2. As summarized in Table 2, this key reaction has been promoted using various heterogeneous catalysts prepared by the immobilization of metallic species on various supports, ranging from halloysite to graphene. On the other hand, both mono and bimetallic systems can be observed in Table 2. Comparison of the yields of aniline, it can be concluded that Pd@CNT-P led to higher or comparable yield of aniline. Comparison of the reaction solvent, it can be found out that compared to some protocols that were promoted in toxic or harsh solvents, the developed protocol that proceeded in water is more favorable from the green chemistry point of view. Regarding the reducing agent, hydrogen gas with low pressure is a safe and environmentally benign reducing agent that is more desirable than chemical reducing agent. Comparing the reaction time and temperature, it can be seen that these values for Pd@CNT-P are comparable with other reported protocols. Considering all of these results as well as the synthetic procedure of the catalyst, it can be concluded that although synthesis of Pd@CNT-P required a multi-step procedure, the resulting catalyst exhibited high catalytic activity in mild reaction condition (low hydrogen pressure and temperature) in aqueous media. Moreover, the catalyst showed high selectivity towards hydrogenation of nitro functionality. On the other hand, the developed procedure can be generalized to highly steric substrates that usually cannot be efficiently hydrogenized in aqueous solution. Furthermore, the required amount of the catalyst was very low (3 wt%) and the recyclability tests (vide infra) confirmed high catalytic recyclability of the catalyst as well as low Pd leaching. Hence, high catalytic performance of the catalyst can compensate multi-step process of the catalyst.

Table 2. Comparison of the catalytic activity of catalyst with the other reported catalysts for the hydrogenation reaction of nitrobenzene.

Entry	Catalyst	Reducing agent	Solvent	Time (h:min)	Temp. (°C)	Yield (%)	Ref
1	Pd@CNT-P	H ₂ (1 atm)	H ₂ O	2	60	100	This work
2	Pd/Hal-H+ CD ^a	H ₂ (1 atm)	H ₂ O	2	50	95	[36]
3	Pd@Hal-pDA-NPC ^b (1 mol%)	H ₂ (1 atm)	H ₂ O	2	50	92	[41]
4	Pd/graphene	NaBH ₄	H ₂ O /EtOH	1:30	50	91	[42]
5	PdCu/C (2 mol% Pd)	NaBH ₄	H ₂ O /EtOH	1:30	50	85	[42]
6	Pd/PPh ₃ @FDU-12 ^c (8.33 × 10 ⁻⁴ mmol Pd)	H ₂ (10 bar)	EtOH	1:00	40	99	[43]
7	Pd NPs/RGO (6 mg)	NaBH ₄	H ₂ O /EtOH	1:30	50	98	[44]
8	Pd ⁰ -AmP-MCF ^d (0.5 mol%)	H ₂ (1 bar)	EtOAc	1.15	r.t.	90	[45]
9	PdNP@PPh ₂ -PEGPIILP ^e (0.05 mol%)	NaBH ₄	H ₂ O	2:00	r.t.	99	[46]

a: Palladated halloysite hybridized with photo- polymerized hydrogel

b: Pd nanoparticles immobilized on the poly-dopamine decorated halloysite nanotubes hybridized with N-doped porous carbon monolayer

c: Pd NPs (1.1 nm) with triphenylphosphine (PPh₃) cross-linked in the nanopore of FDU-12

d: Pd nanoparticles supported on aminopropyl-functionalized siliceous mesocellular foam

e: Palladium nanoparticles stabilized by lightly cross-linked phosphine-decorated polymer immobilized ionic liquids (PIIL) and their PEGylated counterparts (PEGPIIL)

Confirming high catalytic activity of the catalyst, the roles of CD-IL and silica coated CNT in the catalysis were investigated. To start this study, two control catalysts, Pd@CNT-PEGDMA and Pd@P, were prepared. Pd@CNT-PEGDMA that did not contain CD-IL was prepared through polymerization of CNT-A with PEGDMA followed by palladating, while, Pd@P that was a catalyst without silica coated CNT was prepared through polymerization of CD-IL and PEGDMA followed by palladating. In the next step, the catalytic activities of these two catalysts for the hydrogenation of nitrobenzene under the optimum reaction condition were measured and compared with that of the catalyst, Table 3. The results showed that the activity of both control catalysts were inferior compared to that of the main catalyst. To shed light to the origin of this difference, the specific surface area, content of Pd, and Pd average size of both control catalysts were estimated via BET, ICP and TEM, Table 3.

Comparing the structural features of Pd@CNT-PEGDMA and those of the catalyst, it can be seen that the Pd loading of Pd@CNT-P (0.21 mmol g^{-1}) was higher than that of Pd@CNT-PEGDMA (0.11 mmol g^{-1}). According to the literature [47], this observation can be attributed to the contribution of IL to the anchoring of Pd nanoparticles through electrostatic interactions. On the other hand, the specific surface area of Pd@CNT-PEGDMA was slightly larger than that of the catalyst. Considering the Pd average particle size, it can be seen that in Pd@CNT-PEGDMA, this value is slightly lower than that of the catalyst. In other word, in the main catalyst the Pd nanoparticles were slighter larger. According to the literature this issue can be attributed to the presence of IL in the structure of the final catalyst. Considering all these results, it can be concluded that various parameters can affect the catalytic activity of the final catalyst. It can be assumed that lower content of Pd nanoparticles that are the main

catalytic species had the dominant role and led to the lower catalytic activity of Pd@CNT-PEGDMA. Notably, another factor that can result in higher catalytic activity of the catalyst may be the presence of CD in the structure of CD-IL. In more detail, CDs could effectively facilitate transfer of hydrophobic substrates (nitroarenes) into the aqueous media and brings them to the vicinity of Pd nanoparticles and accelerate the reaction [10-22].

In the next step, to explore the role of silica coated CNT in the catalysis, the catalytic activity as well as the structural features of Pd@P were compared with those of Pd@CNT-P. As shown, the specific surface area of this sample is lower than that of the catalyst. This may be due to the relatively high specific surface area of CNT. On the other hand Pd loading of Pd@P is lower than Pd@CNT-P. This can confirm the contribution of silica coated CNT to anchor Pd nanoparticles. Moreover, the Pd average particle size in Pd@CNT-P is smaller than that of Pd@P. This can be attributed to the role of CNT in better dispersion of Pd nanoparticles. The sum of these effects led to the lower catalytic activity of Pd@C compared to that of the catalyst.

Table 3. The comparison of Pd loading, Pd average particle size, specific surface area and catalytic activity of the catalyst with control catalysts ^a.

Entry	Catalyst	S_{BET} (m^2g^{-1})	Pd loading (mmol g^{-1})	Pd average particle size (nm)	Conversion (%)	Yield ^b (%)
1	Pd@CNT-P	61.28	0.21	2.54	100	100
2	Pd@CNT-PEGDMA	66	0.11	2.49	95	87
3	Pd@P	49	0.18	2.67	95	91

a: Reaction condition: nitrobenzene (1 mmol), catalyst (3 wt %) in H₂O (5 mL) as solvent at 60 °C under H₂ atmosphere (1 bar)

b: Isolated yield.

3.3. Study of catalyst recyclability

To check the recyclability of Pd@CNT-P, hydrogenation of nitrobenzene as a model hydrogenation reaction was performed using recovered catalyst for six consecutive reaction runs. In more detail, after recovering the catalyst, Pd@CNT-P was washed, dried and subjected to the next run of the hydrogenation reaction under similar reaction condition. Comparing the efficiency of the catalyst after each run, Figure 7, it was confirmed that Pd@CNT-P retained its catalytic activity for the second reaction run. Upon third reaction run, however, a slight drop of the catalytic activity (5%) was observed. The loss of the catalytic activity was also observed upon further recycling and the yield of aniline reached to 83% after sixth reaction run. These results confirmed high recyclability of Pd@CNT-P. To elucidate whether recycling induced significant Pd leaching, the recycled catalysts were subjected to ICP analysis. The ICP results confirmed that upon the first four recycling, Pd leaching was insignificant (0.4 wt% of the initial loading). Upon further recycling, the Pd leaching increased and reached to 8 wt% of initial Pd loading after sixth run.

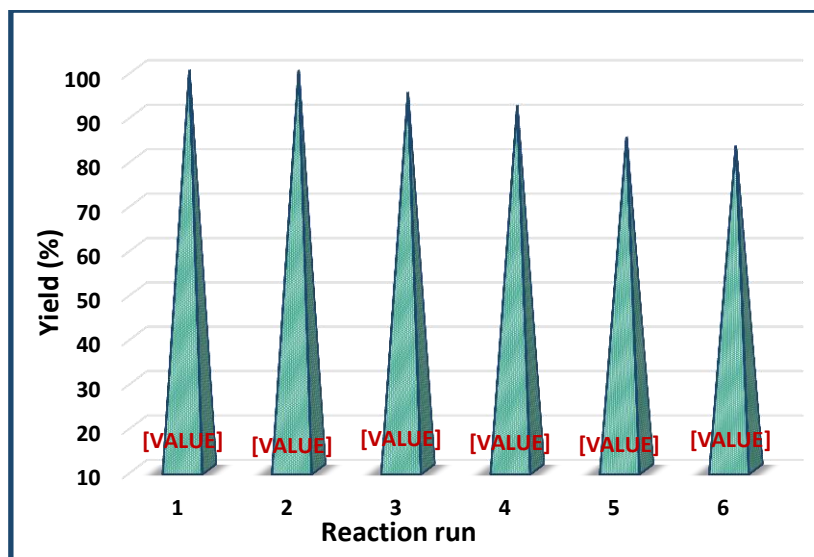


Figure 7. The recycling results for hydrogenation of nitrobenzene under optimum reaction condition.

Next, to verify whether recycling of the catalyst could result in destruction of the structure of the catalyst, the FTIR spectrum of the recycled catalyst after six reaction run under optimum reaction condition was recorded and compared with that of fresh Pd@CNT-P. As depicted in Figure 8, both recycled and fresh catalysts showed similar FTIR spectrum, confirming that Pd@CNT-P preserved its structure upon recycling.

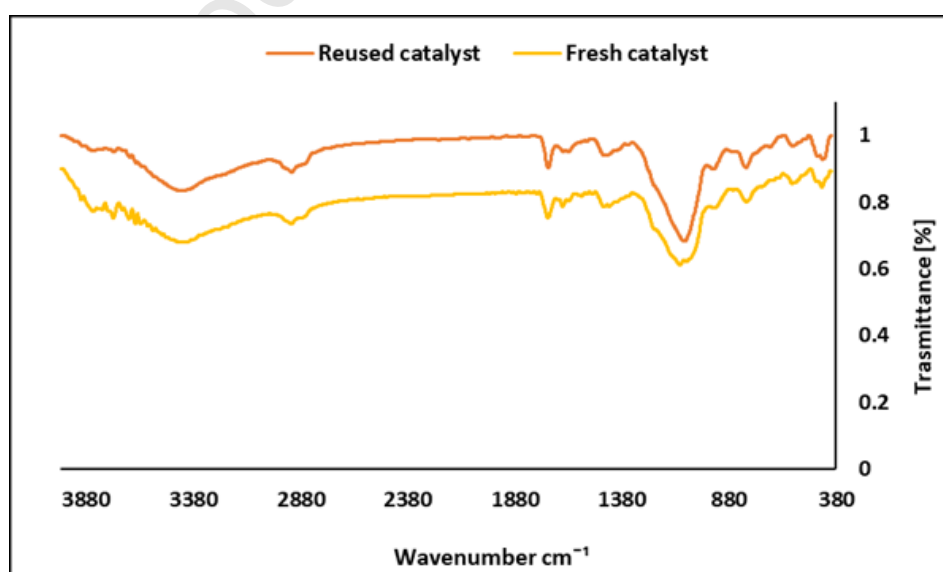


Figure 8. The FTIR spectra of fresh and recycled catalyst after six reaction run of hydrogenation of the model reaction under the optimum reaction condition.

To explore the possible change of the catalyst morphology and Pd particle size upon recycling, the TEM images of the recycled catalyst after six runs of the hydrogenation of the model reaction under optimum reaction condition were recorded, Figure 9. As illustrated, recycling did not change the morphology of the catalyst. Moreover, estimation of Pd nanoparticles confirmed that the average Pd nanoparticle size was 2.61 ± 0.91 that was very close to that of the fresh catalyst, confirming that recycling did not induce Pd aggregation.

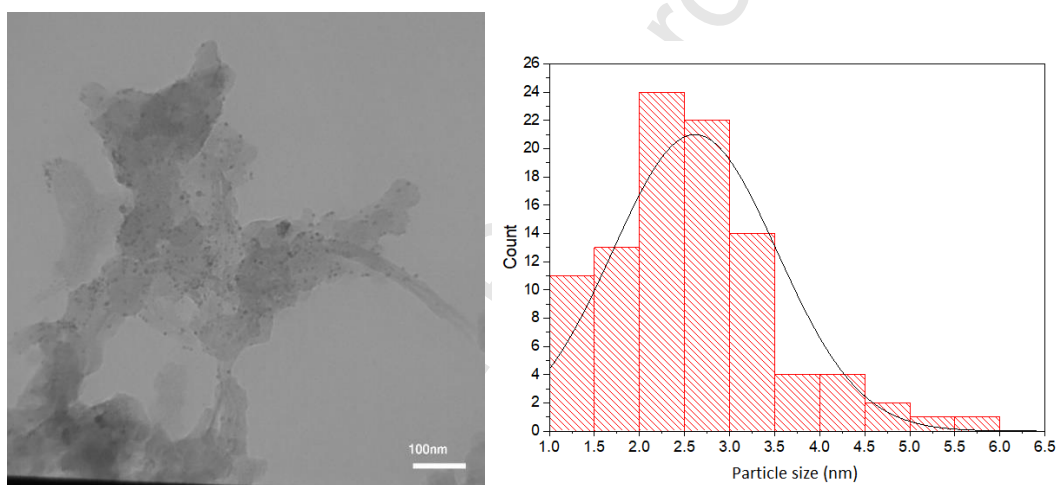


Figure 9. TEM image of the recycled catalyst after six reaction run of hydrogenation of the model reaction under the optimum reaction condition and the histogram for Pd particle size.

Considering all of these results, the loss of the catalytic activity of the recycled catalyst can be assigned to the Pd leaching.

3.4. Hot filtration test

In the following, the nature of the catalysis was elucidated through hot filtration method. The results confirmed that in the course of the hydrogenation reaction, Pd nanoparticles did not

leach to the reaction media. In other word, by halting the reaction in short time interval and separation of the catalyst, the hydrogenation reaction in the filtrate stopped and did not proceed anymore, indicating the heterogeneous nature of the catalysis.

Conclusion

With the aim of benefiting from the chemistry of IL, CNT and CD, a functional polymer, CNT-P was designed and prepared via multi-step procedure. In detail, CNT was first coated with silica layer and then vinyl functionalized. Then, CD-IL was simply prepared through reaction of vinyl imidazole and tosylated CD. In the final stage, the polymerization reaction of CD-IL, CNT and PEGDMA resulted in the formation of CNT-P. The latter was then palladated and applied as a heterogeneous catalyst for promoting hydrogenation of nitroarenes in aqueous media. The results confirmed high catalytic activity and selectivity of the catalyst. Furthermore, the catalyst could be recycled for six reaction runs. The high catalytic activity of the catalyst in aqueous media was attributed to several factors. First, CD in the structure of the catalyst could act as a phase transfer agent and accelerate the reaction in the aqueous media. Secondly, the multiple functional groups on the polymeric part could enhance loading of Pd nanoparticles that are the main catalytic active species and consequently improve the catalytic activity of the resulting hybrid system. Silica coated CNT on the other hand, can provide high dispersion of Pd nanoparticles. Notably, the comparison of the catalytic performance of the catalyst with some previously developed catalysts confirmed high activity of Pd@CNT-P under mild reaction condition and aqueous media. This feature along with high selectivity, recyclability and low Pd leaching of the catalyst compensated the multi-step synthetic protocol of Pd@CNT-P.

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The roles of the authors for preparation of this article is as follow:

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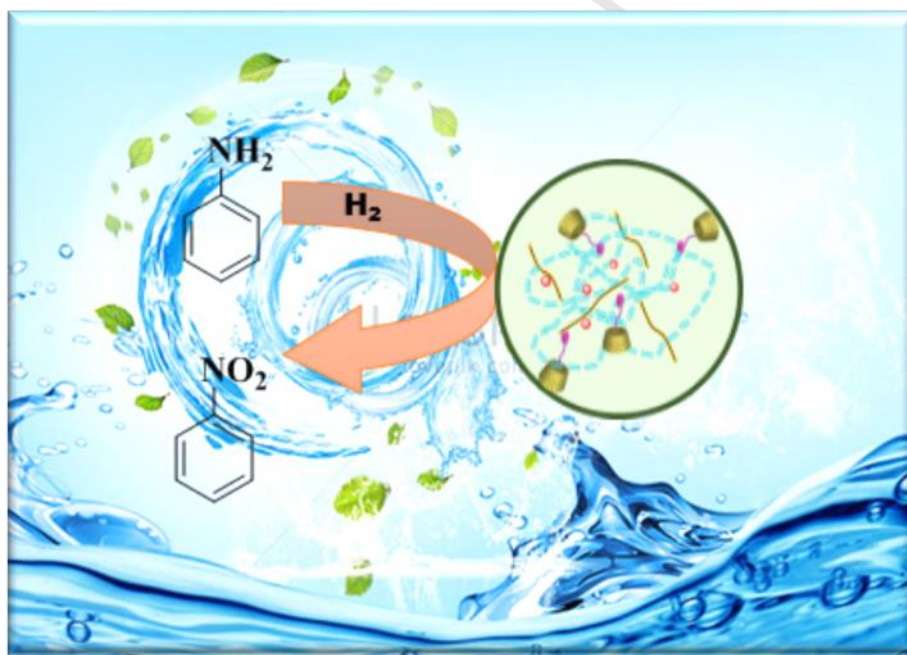
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Journal Pre-proof

Pd immobilized on polymeric network containing imidazolium salt, cyclodextrin and carbon nanotubes: efficient and recyclable catalyst for the hydrogenation of nitroarenes in aqueous media

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Highlight

- A functional polymer containing imidazolium salt, CNT and cyclodextrin is prepared.
- Palladated polymeric system was used as a heterogeneous hydrogenation catalyst.
- The catalyst was selective and recyclable.
- Cyclodextrin could act as phase transfer agent to allow the reaction to proceed in water.
- Imidazolium salt and CNT improved anchoring and dispersion of Pd nanoparticles.