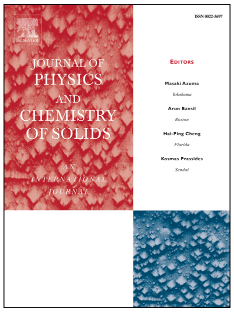

Pd/$CoFe_2O_4$/chitosan: A highly effective and easily recoverable hybrid nanocatalyst for synthesis of benzonitriles and reduction of 2-nitroaniline

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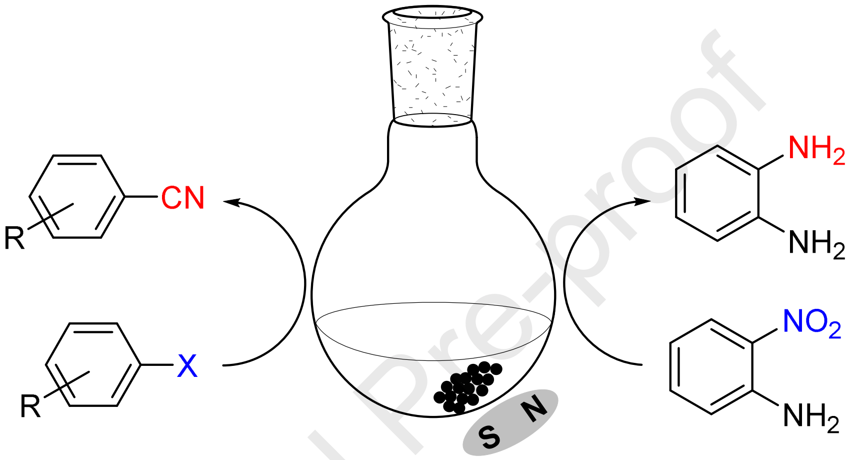
Graphical Abstract

Pd/$CoFe_2O_4$/chitosan: A highly effective and easily recoverable hybrid nanocatalyst for synthesis of benzonitriles and reduction of 2-nitroaniline

Talat Baran and Mahmoud Nasrollahzadeh[*]



Pd/$CoFe_2O_4$/Chitosan hybrid nanocatalyst

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Pd/$CoFe_2O_4$/chitosan: A highly effective and easily recoverable hybrid nanocatalyst for synthesis of benzonitriles and reduction of 2-nitroaniline

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Abstract

In this study, a novel catalyst system with high activity and easy recoverability was successfully prepared through the deposition of Pd nanoparticles (NPs) onto designed sustainable hybrid beads containing magnetic cobalt ferrite and chitosan (Pd/$CoFe_2O_4$/chitosan). The catalytic potential of Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst was then assessed in i) preparation of benzonitriles *via* aryl halides cyanation and ii) reduction of 2-nitroaniline (2-NA). Various aryl iodides and bromides were successfully cyanated by Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst with excellent reaction yields within 3 h. In addition to the production of benzonitriles, the hybrid nanocatalyst showed excellent activity by reducing 2-NA in 65 s. It was proved that the Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst outperformed many catalysts used in the cyanation of aryl halides and catalytic reduction of 2-NA previously reported in the literature. Moreover, it was found that the designed

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Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst was easily and effectively separated from the reaction mixture using an external magnet and reused several times in catalytic reactions without considerable loss of catalytic activity.

Keywords: Pd catalyst, Chitosan, Benzonitrile, 2-Nitroaniline

1. Introduction

Recently, generation of noble metal nanocatalysts has attracted the attention of scientists due to their excellent catalytic performance, nanosized structures, good electronic/optical properties and huge surface areas [1, 2]. Therefore, different noble metals have been designed as homogeneous or heterogeneous nanocatalysts for different organic reactions [3, 4]. Although homogeneous catalysts are highly effective and selective, they suffer from separation problems and usually need costly and specific separation techniques [5, 6]. To address this problem, preparation of heterogeneous catalysts on various organic/inorganic support materials has recently received significant attention due to the facile separation of catalysts [7-9]. However, in most cases, the recovery of heterogeneous catalysts from the reaction medium *via* simple traditional methods such as filtration and centrifugation is a tedious and time consuming task. These problems can be eliminated by the preparation of catalysts on the modified magnetic composites as catalyst supports to obtain easily separable catalyst [9, 10]. Additionally, catalysts with magnetic nature can be reused several times due to retaining their initial activity, which makes them sustainable and ideal catalysts in organic reactions. Modified magnetic composites are usually prepared on a magnetic core and then modified with various compounds to obtain different stabilizers/supports [11, 12].

The development of magnetically recoverable catalytic systems from the reaction media without using conventional costly and tedious work-up methods plays a crucial role in both organic reactions and industrial applications. Among magnetic NPs, cobalt spinel ferrites ($CoFe_2O_4$) have superior properties such as high magnetization, excellent mechanical and chemical stability as well as easily modified surfaces [13, 14]. Therefore, various compounds can be combined with $CoFe_2O_4$ to synthesize catalyst supports. Chitosan, which is a versatile and renewable biopolymer obtained from natural sources, has outstanding properties such as biocompatibility, low cost, abundance and high thermal stability [15, 16]. More importantly, it has free hydroxyl and amine functional groups, which can provide coordination of transition metals on the polymer backbone [17]. Additionally, chitosan hydrogel beads can be easily obtained *via* these functional groups to improve the metal binding capacity of chitosan [18]. There are several reports concerning the application of chitosan based magnetic catalysts in organic synthesis [19-21]. Therefore, chitosan can be modified with $CoFe_2O_4$, followed by the preparation of $CoFe_2O_4$/chitosan hybrid beads as stabilizers. Afterwards, different metallic nanoparticles can be immobilized on the designed support and their catalytic role in various organic reactions can be investigated.

Benzonitriles are important structural moieties of several valuable compounds such as agrochemicals, biologically active compounds, natural products and dyes [4,22]. Moreover, these versatile compounds can be readily transformed into different functional groups such as aldehydes, amides, acids, amines and ketones [4,22]. For more than a century, benzonitriles have been synthesized by Rosenmund-von Braun and Sandmeyer reactions [23-26]. However, these traditional methods suffer from some disadvantages such as i) high reaction temperatures, ii) large quantities of heavy metal wastes and iii) use of stoichiometric amounts of CuCN [27, 28]. Therefore, transition metal catalyzed aryl halide cyanation reactions have been developed as a new methodology for the synthesis of benzonitriles using cyanating agents such as $Cu(CN)_2$, NaCN, KCN, TMSCN, $Zn(CN)_2$ etc. [4,29-31]. However, the application of many cyanide agents is generally limited in in the industry due to their highly toxic nature [4, 30]. Therefore, there is a need for a low toxic cyanation source in this reaction. Recently, $K_4[Fe(CN)_6]$ has been utilized as a cyanation agent by researchers due to its inexpensiveness, non-toxicity, safety, simplicity of handling and commercial availability [27, 32]. Different metal catalysts have been designed and utilized in the aryl halide cyanation in the presence of $K_4[Fe(CN)_6]$ [33, 34]. Owing to their high catalytic activity and excellent functional group tolerance, Pd catalysts play an important role in this reaction compared to the other metal catalysts [30, 35]. Pd catalysts with efficient catalytic performance are thus highly desired in the cyanation of aryl halides.

Nowadays, water and environmental pollution caused by various organic pollutants; especially nitro compounds, has become an important issue [36, 37]. Among nitro compounds, 2-nitroaniline (2-NA) is one of the most dangerous compounds for aquatic and human life due to its potential mutagenic and carcinogenic effects [38]. Therefore, 2-NA poses a great threat to both environmental and public health even at very low concentrations in water [39]. Hence, the removal of 2-NA from environmental waters is vital to protect human health. Up till now, different strategies such as thermal decomposition, photocatalytic degradation, adsorption and catalytic reduction have been developed to remove nitro compounds [36, 40-42]. Among these, catalytic reduction is one of the most preferable processes since it provides easy operation, high performance and cost effectiveness [43, 44]. Additionally, catalytic reduction products can be used in various areas. For example, *o*-phenylenediamine, which is the reduction product of *o*-NA, has been widely utilized in the synthesis of different products such as surfactants, polymers and dyes [45-47]. Therefore, the reduction of *o*-NA to *o*-phenylenediamine in the presence of catalysts is also of great importance both in terms of environmental and industrial issues and catalysts with high performance are greatly desired in this reaction.

In this study, a new heterogeneous Pd nanocatalyst was prepared on magnetic hybrid microbeads consisting of $CoFe_2O_4$/chitosan as the support and its chemical structure was characterized by FT-IR, FE-SEM, EDS, TEM and XRD. Based on the characterizations,

$Pd/CoFe_2O_4$/chitosan was homogeneously dispersed with a particle size of about 25 nm. The catalytic behavior of $Pd/CoFe_2O_4$/chitosan hybrid nanocatalyst was then investigated in i) aryl halide cyanation and ii) 2-NA reduction. $Pd/CoFe_2O_4$/chitosan hybrid nanocatalyst showed high catalytic performance in the halide cyanation with a high reaction yield of up to 98%. $Pd/CoFe_2O_4$/chitosan hybrid nanocatalyst developed also successfully converted *o*-NA to *o*-phenylenediamine within a very short reaction time (65 s). More importantly, $Pd/CoFe_2O_4$/chitosan hybrid nanocatalyst displayed high reusability in both aryl halide cyanation and *o*-NA reduction due to its magnetic recoverability.

3. Results and discussion

2. Experimental

2.1. Tools and reagents

Chitosan (De-acetylation degree: 78%, low molecular weight), $FeCl_3.6H_2O$, $CoCl_2.6H_2O$, glutaraldehyde, $PdCl_2$, 2-nitroaniline, $K_4[Fe(CN)_6]$, $NaBH_4$, Na_2CO_3, KOH, NaOH, Cs_2CO_3, K_2CO_3, DMF, DMSO, NMP, toluene and aryl halides were purchased from Sigma-Aldrich Chemical Co. The FT-IR spectra of $CoFe_2O_4$/chitosan and $Pd/CoFe_2O_4$/chitosan nanocatalyst were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrophotometer. The XRD patterns of $CoFe_2O_4$, $CoFe_2O_4$/chitosan and $Pd/CoFe_2O_4$/chitosan hybrid nanocatalyst were obtained using a Rigaku smart lab system. The FE-SEM micrograms and EDS images of $CoFe_2O_4$/chitosan and $Pd/CoFe_2O_4$/chitosan hybrid nanocatalyst were obtained using a QUANTA-FEG 250ESEM. The TEM images of $Pd/CoFe_2O_4$/chitosan hybrid nanocatalyst were recorded by a TEM JEOL JEM-2100 (UHR) instrument. The reduction of 2-NA was followed by UV-Vis spectroscopy (Genesys 10S UV-Vis spectrophotometer). Benzonitriles were characterized using a GC-MS Agilent GC-7890 A-MS 5975 instrument.

2.2. Synthesis of $CoFe_2O_4$

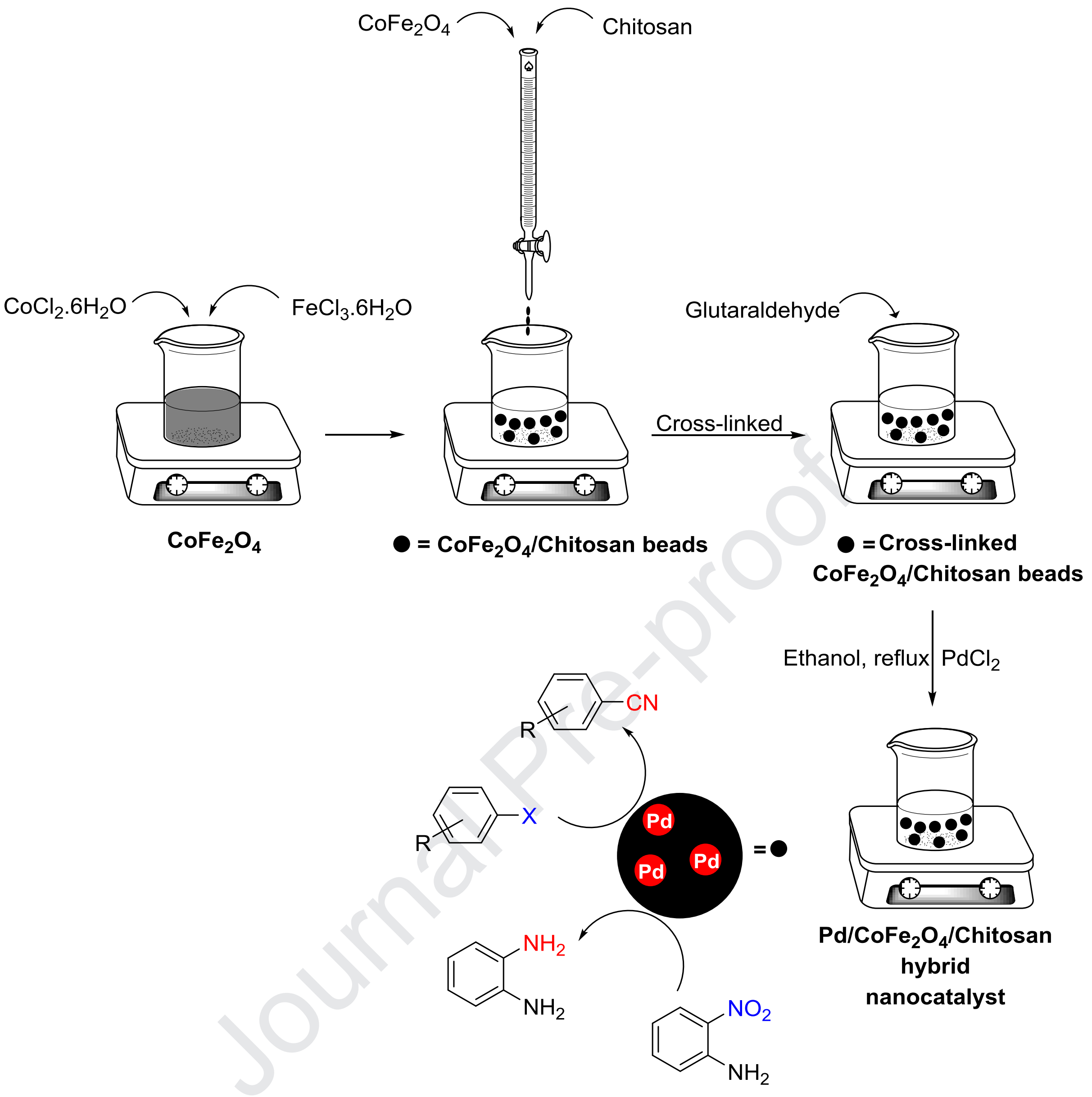
$FeCl_3.6H_2O$ (8.2 mmol) and $CoCl_2.6H_2O$ (4.1 mmol) were dissolved in 75 mL of water and the solution obtained was stirred at room temperature (RT). 3 g of NaOH (15 mL) were then added to the reaction mixture dropwise over a period of 10 min during which a black colored precipitate was formed. Afterwards, the reaction temperature was increased to 90 °C and stirring was continued for 2 h. Finally, the mixture was cooled to RT and magnetic particles were then collected by an external magnet, rinsed with water, dried at 80 °C overnight and calcined at 500 °C for 5 h (Scheme 1).

2.3. Synthesis of $CoFe_2O_4$/chitosan hybrid beads as stabilizer

1 g of chitosan was dissolved in acetic acid solution (100 mL, 2% v/v) at RT, followed by the addition of 1 g of $CoFe_2O_4$ and stirring for 3 h. The resulting mixture was poured into an alkaline solution containing NaOH (12 g), water (40 mL) and methanol (60 mL) to form spherical gel beads. $CoFe_2O_4$/chitosan hydrogel beads were then recovered by filtration and washed with water. Cross-linking was performed by stirring $CoFe_2O_4$/chitosan hydrogel beads with glutaraldehyde (3 mL) in 50 mL of methanol at 70ºC for 6 h. Finally, the cross-linked $CoFe_2O_4$/chitosan beads were collected, washed with water and dried to use as a catalyst support in the synthesis of Pd NPs (Scheme 1).

2.3. Preparation of Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst

1.5 g of the designed $CoFe_2O_4$/chitosan microcapsules and 0.3 g of $PdCl_2$ were added into 30 mL of ethanol and the mixture obtained was stirred 70 °C for 4 h. At the end of this period, Pd/$CoFe_2O_4$/chitosan nanocatalyst was collected using an external magnet, washed with ethanol and dried to test its catalytic performance in both aryl halide cyanation and 2-NA reduction (Scheme 1).



Scheme 1. Preparation of Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst.

2.4. Typical procedure for aryl halide cyanation using Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst

To a Schlenk tube, aryl halide (1.0 mmol), Na_2CO_3 (1.5 mmol), $K_4[Fe(CN)_6]$ (0.2 mmol), Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst (0.25 mol. %) and DMF (6 mL) were transferred and the resulting mixture was stirred at 120 °C for 3 h. At the end of cyanation reaction, Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst was separated by an external magnet from the reaction medium. The reaction mixture was then extracted using H_2O: diethyl ether mixture three times and the organic phase, which contained benzonitriles, was dried over Na_2SO_4. Finally, the desired benzonitrile products were obtained by evaporating the solvents and benzonitriles were characterized by FT-IR and GC-MS (Fig. S1-S7) analyses.

2.5. Reduction of 2-NA catalyzed by Pd/CoFe$_2$O$_4$/chitosan hybrid nanocatalyst

Freshly prepared $NaBH_4$ (0.1 mL, 2.5×10^{-2} M) was added to a 2-NA solution (1 mL, 1.25×10^{-4} M) and the resulting mixture was stirred at RT for 2 min. Afterwards, Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst (4 mg) was added to the mixture and stirring was continued until completion of 2-NA reduction. The progress of the conversion of 2-NA to *o*-phenylenediamine was monitored by UV-Vis spectroscopy. After the 2-NA reduction was complete, Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst was easily separated using an external magnet, washed with water and dried to use in recycling studies.

3. Results and discussion

3.1 Characterization of Pd/CoFe$_2$O$_4$/chitosan hybrid nanocatalyst

Fig. 1 shows the comparative FT-IR spectra of $CoFe_2O_4$/chitosan and Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst. In the spectrum of $CoFe_2O_4$/chitosan, characteristic adsorption peaks were observed at 3293 cm^{-1} (-OH stretching), 2923-2874 cm^{-1} (-CH stretching), 1556 cm^{-1} (-NH bending vibration), 1403 cm^{-1} (-C-H stretching), 1012 cm^{-1} (-C-O-C stretching) [48]. Moreover, a new peak was observed at 1638 cm^{-1}, which corresponded to the stretching of the imine group, confirming the formation of $CoFe_2O_4$/chitosan beads. Although the FT-IR spectrum of Pd/$CoFe_2O_4$/chitosan is similar to that of its support $CoFe_2O_4$/chitosan), it was observed that the peaks corresponding to the functional groups of $CoFe_2O_4$/chitosan shifted to lower wavelengths because of interaction of palladium with $CoFe_2O_4$/chitosan microbeads. On the other hand, the FT-IR analysis of samples was carried out using ATR-FT-IR (4000-

650 cm^{-1}). The characteristic Fe bands, which generally occur at low wavenumbers (<600 cm^{-1}), were not observed in the spectrum. Therefore, the presence of Fe peaks confirmed the results of XRD and EDS analyses.

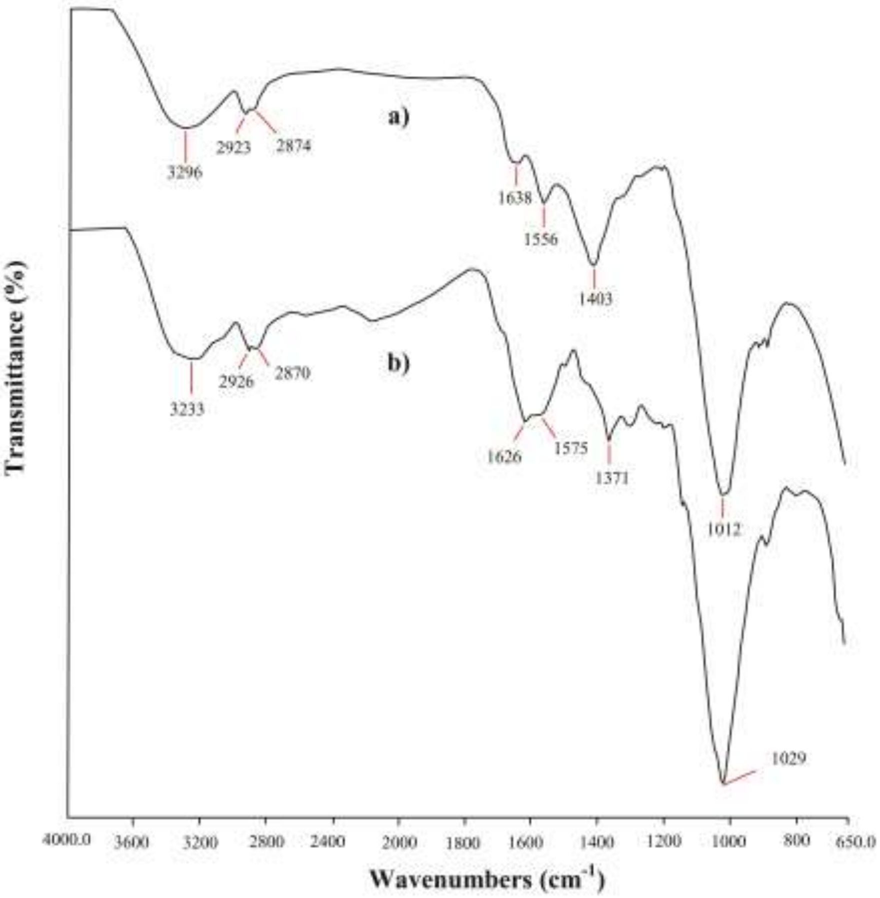


Fig. 1. FT-IR spectra of $CoFe_2O_4$/chitosan (a) and Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst (b).

The XRD patterns of $CoFe_2O_4$, $CoFe_2O_4$/chitosan and Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst are shown in Fig. 2. The XRD spectrum of $CoFe_2O_4$ displayed typical diffraction peaks at 18.25º, 30.14º, 35.55º, 43.11º, 53.75º, 57.06º and 62.68º, which are assigned to [111], [220], [311], [400], [422], [511] and [440] planes of $CoFe_2O_4$, respectively [49, 50]. These peaks confirmed the successful fabrication of $CoFe_2O_4$. Following the synthesis of $CoFe_2O_4$/chitosan microbeads, a new broad peak was observed at 20.06º, which was due to chitosan [17]. As for the XRD pattern of Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst, five new diffraction peaks were clearly observed at 40.15°, 46.66°, 68.12°, 82.06° and 86.50°, which are attributed to (111), (200), (220), (311) and (222) crystalline planes of face-centered palladium, respectively, confirming the fabrication of Pd NPs on $CoFe_2O_4$/chitosan microbeads [51].

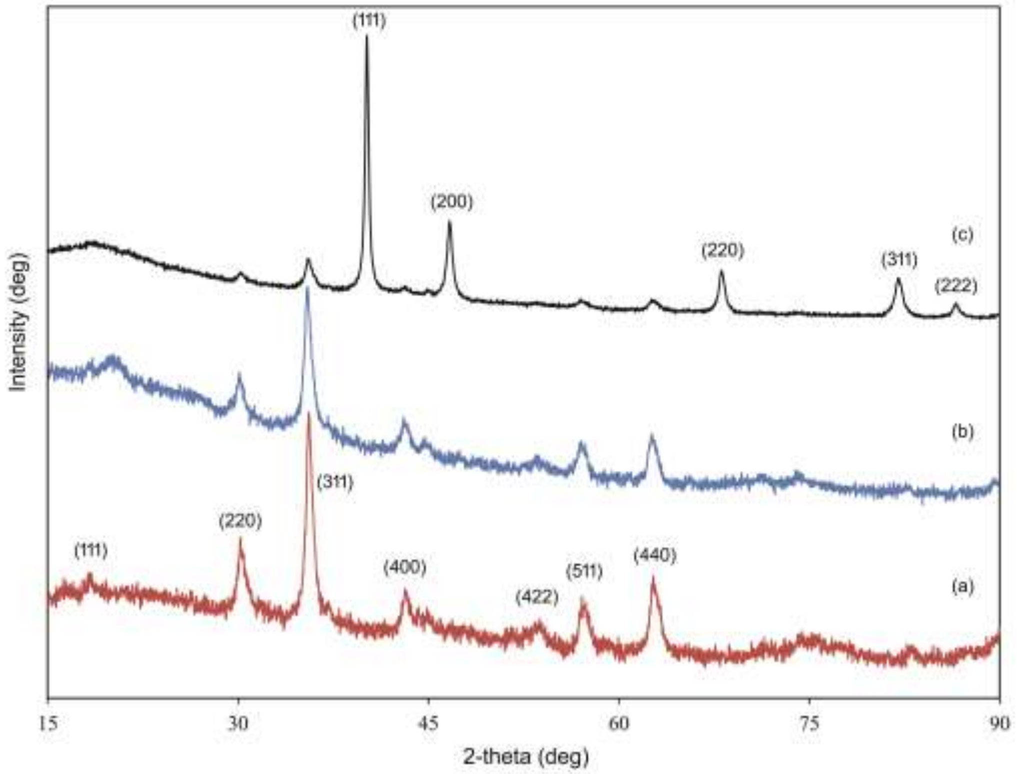


Fig. 2. XRD patterns of $CoFe_2O_4$ (a), $CoFe_2O_4$/chitosan (b) and Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst (c).

Fig. 3 demonstrates the SEM images of the $CoFe_2O_4$/chitosan and Pd/$CoFe_2O_4$/chitosan hybrid nanocatalysts, respectively. SEM images evidently indicated that both $CoFe_2O_4$/chitosan and Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst had spherical morphologies, confirming the formation of their microbead form (Fig. 3a, c). Additionally, the surface morphologies of $CoFe_2O_4$/chitosan and Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst beads were investigated at higher magnifications. The images showed that both cobalt ferrite and Pd NPs were fabricated (Fig. 3b,d). On the other hand, the elemental compositions of $CoFe_2O_4$/chitosan and Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst beads were studied by EDS analysis (Fig. 4). The EDS spectrum of $CoFe_2O_4$/chitosan beads showed the presence of C, N, O, Fe and Co peaks (Fig. 4a). In the EDS spectrum of Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst, Pd element was clearly observed, indicating the production of Pd nanocatalyst on the support ($CoFe_2O_4$/chitosan) (Fig. 4b)

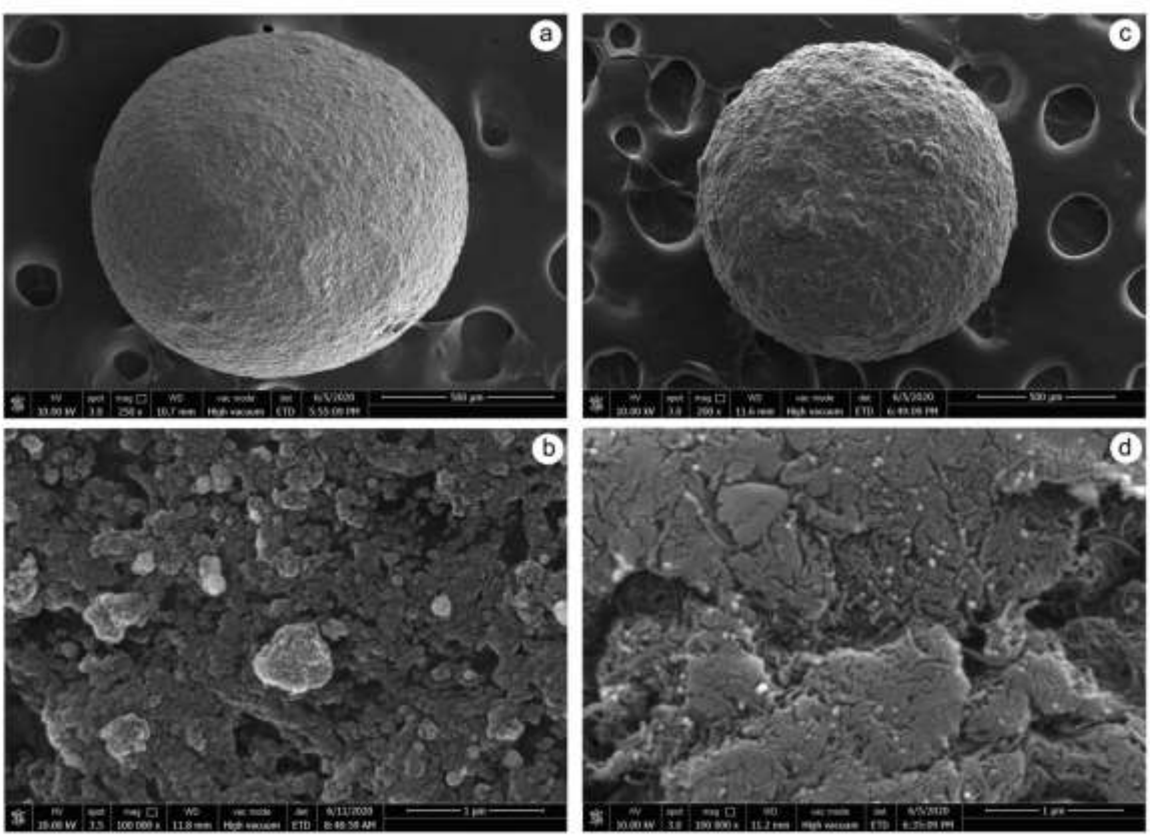


Fig. 3. SEM micrograms of $CoFe_2O_4$/chitosan (a,b) and Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst (c,d).

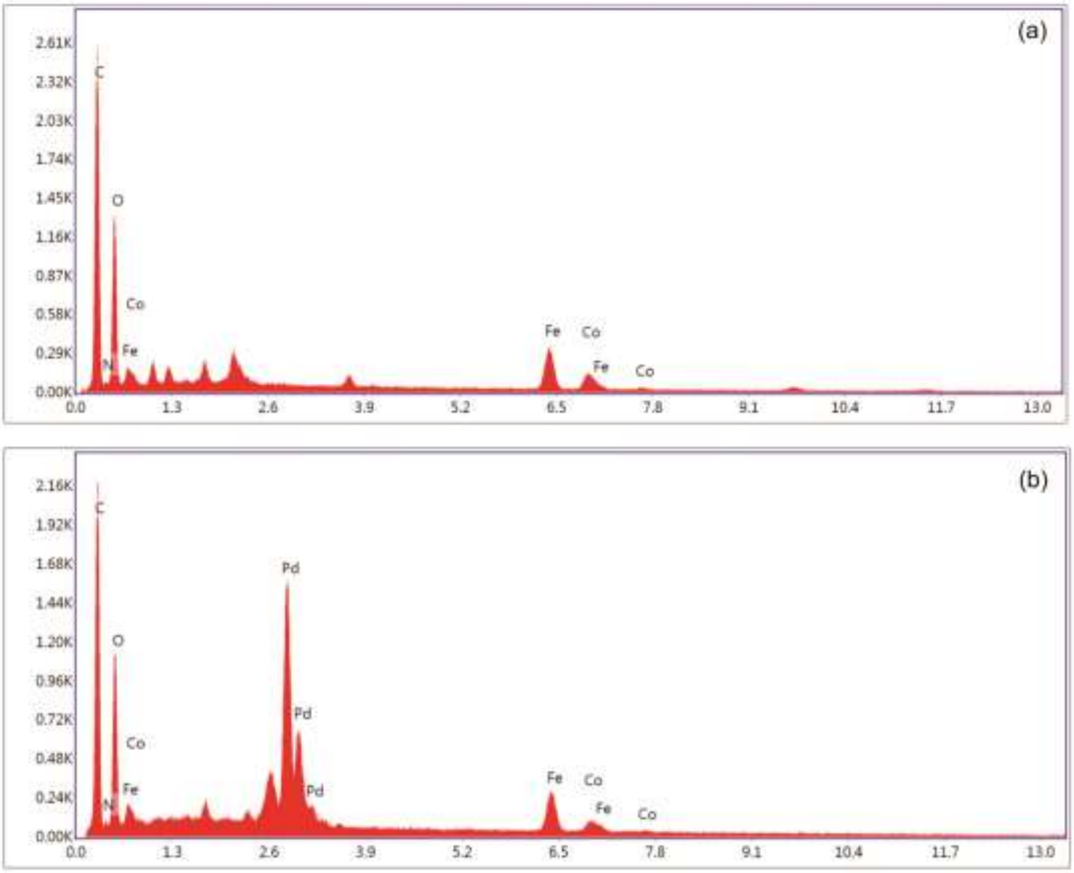


Fig. 4. EDS spectra of $CoFe_2O_4$/chitosan (a) and Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst (b).

The TEM analysis of Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst beads was performed for further characterization and the obtained TEM images are shown in Fig. 5. The TEM images showed that Pd NPs were successfully immobilized on $CoFe_2O_4$/chitosan and their average diameter were around ~20 nm.

The content of the Pd within Pd/$CoFe_2O_4$/chitosan, as determined by ICP-OES (Inductively coupled plasma-optical emission spectrometry), was found to be 9.36 wt%.

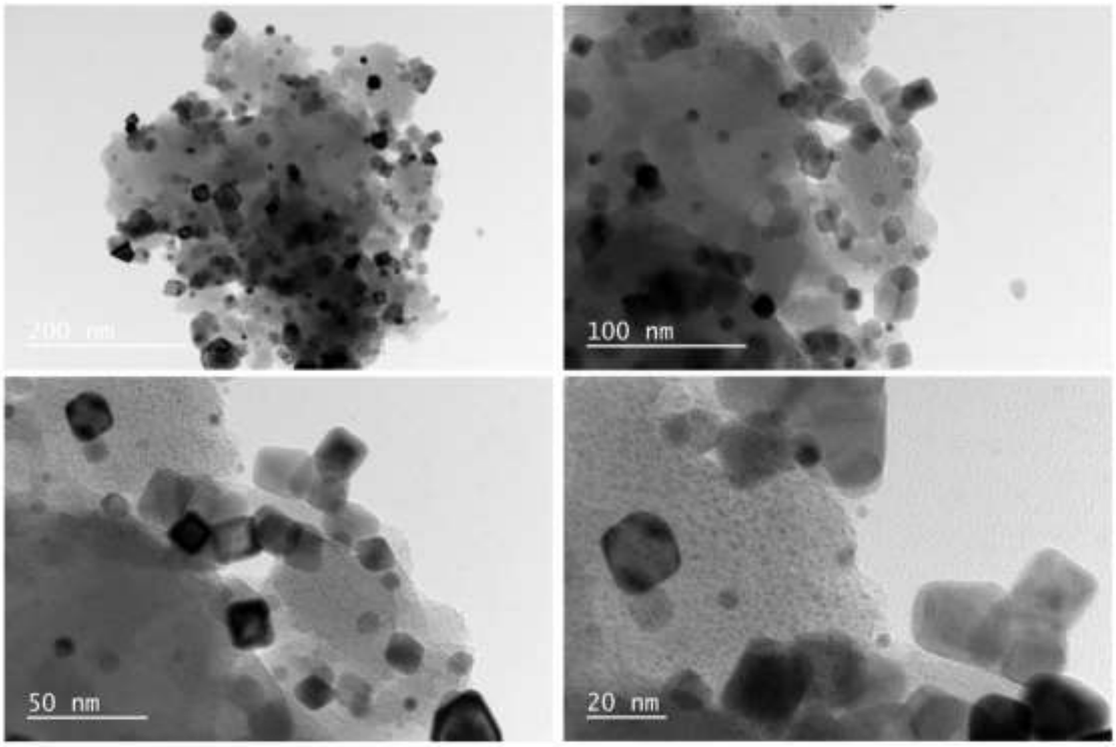


Fig. 5. TEM images of Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst.

3.2. Investigation of catalytic activity of Pd/$CoFe_2O_4$ chitosan hybrid nanocatalyst

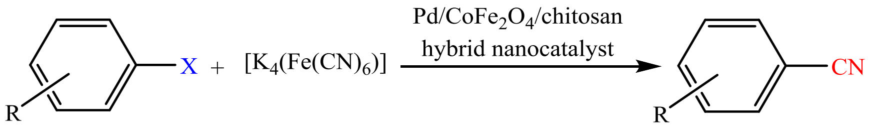
The catalytic behavior of Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst was first evaluated in aryl halide cyanation in the presence of $K_4[Fe(CN)_6]$, which is a cyanide source with low toxicity, cost effectiveness and ready availability. To optimize the reaction parameters, the cyanation of p-$NO_2C_6H_4Br$ by Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst was chosen as the model reaction. Preliminary experiments were then performed under various reaction conditions and the isolated yields are listed in Table 1. Based on the results of the control experiment, the optimal reaction conditions were as follows; catalyst loading: 0.25 mol. %, base: Na_2CO_3, solvent: DMF, reaction temperature: 120 °C and reaction time: 3 h. The scope of activity of Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst was then studied in the cyanation of a range of aryl halides under optimal conditions and the results are summarized in Table 2. The results showed that both aryl iodide and bromide cyanation reactions proceeded smoothly with good reaction yields in the presence of Pd/$CoFe_2O_4$/chitosan nanocatalyst. In addition, Pd/$CoFe_2O_4$/chitosan was an effective nanocatalyst with a broad range of substrates in aryl halide cyanation. Additionally, the catalytic efficacy of Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst was compared to that of other reported catalysts in the cyanation of *p*-$CH_3C_6H_4I$ and the results are given in Table 3. As observed in the Table, the developed catalyst system (Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst) is superior to the other reported systems in terms of yield, amount of catalyst and reaction time.

Table 1. The optimization of reaction conditions for cyanation of *p*-$NO_2C_6H_4Br$ using $K_4[Fe(CN)_6]$.

Entry	Catalyst (mol%)	Solvent	Base	Time (h)	Yield (%)
1	0.25	Toluene	K_2CO_3	2	70
2	0.25	DMF	K_2CO_3	2	82
3	0.25	NMP	K_2CO_3	2	65
4	0.25	DMSO	K_2CO_3	2	45
5	0.25	DMF	KOH	2	45
6	0.25	DMF	NaOH	2	52
7	0.25	DMF	Na_2CO_3	2	88
8	**0.25**	**DMF**	**Na_2CO_3**	**3**	**98**
9	0.1	DMF	Na_2CO_3	3	78
10	0.3	DMF	Na_2CO_3	3	98
11	0	DMF	Na_2CO_3	3	0

Reaction conditions: *p*-$NO_2C_6H_4Br$ (1.5 mmol), $K_4Fe(CN)_6$ (0.2 mmol), base (1.8 mmol), DMF (6.0 mL), 120 °C.

Table 2. Catalytic role of Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst in the synthesis of benzonitriles.



Entry	R	X	Yield[a] (%)
1	m-NO_2	I	97
2	*p*-CH_3O	I	95
3	*p*-CH_3	I	93
4	*m*-CH_3	I	91

5	*o*-CH_3	I	90
6	*m*-NO_2	Br	96
7	*p*-NO_2	Br	98
8	*p*-CH_3O	Br	94
9	*p*-CN	Br	99
10	*p*-CH_3	Br	92
11	*m*-CH_3	Br	89
12	*o*-CH_3	Br	88

Reaction conditions: aryl halides (1.5 mmol), $K_4Fe(CN)_6$ (0.2 mmol), Na_2CO_3 (1.8 mmol), Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst (0.25 mol %), DMF (6.0 mL), 3h, 120 °C.

[a] Isolated yields.

Table 3. Comparison of Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst with other reported catalysts in the cyanation of *p*-$NO_2C_6H_4Br$.

Entry	**Catalyst**	**Time**	**Yield (%)**	**Ref.**
1	Pd@$CuFe_2O_4$	24 h	78	[21]
2	Pd-CD-PU-NS	10 h	89	[52]
3	Pd-LHMS-3	12 h	85	[53]
4	Pd NPs	7h	85	[54]
5	Pd/PPy nanocomposite	6h	93	[31]
6	Pd NPs@CAP	8h	95	[55]
7	Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst	3h	98	Present study

On the other hand, the catalytic performance of Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst was also investigated in 2-NA reduction in water at room temperature using $NaBH_4$ as the hydrogen source. 2-NA reduction in the presence of Pd/$CoFe_2O_4$/chitosan nanocatalyst was followed by UV-Vis spectroscopy. It is known that 2-NA has typical UV-Vis bands of λ_{max} at about 283 nm and 410 nm [56]. It was reported that following the reduction of 2-NA i) the band at 410 nm diminished and ii) the band at ~283 nm shifted to higher wavelength due to the formation of *o*-phenylenediamine [57]. In this study, as observed in Fig. 6a, 2-NA gave two characteristic absorption bands at 283 nm and 400 nm in the absence of Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst. After adding the prepared

Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst into the reaction mixture containing 2-NA and $NaBH_4$, the adsorption band of 2-NA at 410 nm gradually decreased as the catalytic reaction proceeded and completely disappeared within 65 s. Additionally, it was observed that the yellow color of the reaction mixture solution converted into colorless as the reaction continued. Moreover, the band at 283 nm shifted to 292 nm, confirming the formation of *o*-phenylenediamine. These observations showed that 2-NA was successfully converted to *o*-phenylenediamine by Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst within 65 s. On the other hand, the control experiment was performed in the absence of Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst and no reduction product was observed at extended period of time in the UV-Vis spectrum. This indicated that Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst was critically important in the 2-NA reduction.

Fig. 6b displayed shows a linear correlation between ln (c/c_0) and reaction time (t) for 2-NA reduction using Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst. Since $NaBH_4$ concentration is higher than that of 2-NA, the catalytic system follows pseudo first order kinetics. The rate constant was calculated as 0.0131s^{-1} using the following equation:

$$\ln (c/c_0) = -kt$$

where, c_0 and c are the initial concentrations of 2-NA at tested reaction time (t), and also k (s^{-1}) is the reaction rate.

It has been reported that ferrites NPs are important magnetic materials, which are used for various applications such as drug delivery, magnetothermal therapy, microwave absorbent sensors, and as catalysts in for many organic transformations [58,59]. However, among the nanoparticles, Pd NPs stand out as effective catalysts due to their high activity and stability in different organic reactions. For further investigation, the activity of Pd/$CoFe_2O_4$/chitosan nanocatalyst was compared to that of $CoFe_2O_4$/chitosan nanocatalyst. Cyanation of *p*-

$NO_2C_6H_4Br$, which was selected as the model reaction, was carried out in the presence of $CoFe_2O_4$/chitosan nanocatalyst under optimal reaction conditions (Na_2CO_3, DMF, 120 °C, 3 h etc.) and a very low yield was obtained (~3%). On the other hand, the reduction of 2-NA in the presence of $CoFe_2O_4$/chitosan nanocatalyst was complete after 15 min. These results show that the designed Pd/$CoFe_2O_4$/chitosan nanocatalyst is critically significant in the cyanation of aryl halides and 2-NA reduction.

To show the superiority of Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst, its catalytic efficiency was compared with that of some reported catalysis in 2-NA reduction (Table 4). According to the results, Pd/$CoFe_2O_4$/chitosan is a more effective catalyst than other catalysts in terms of reaction time and catalyst amount.

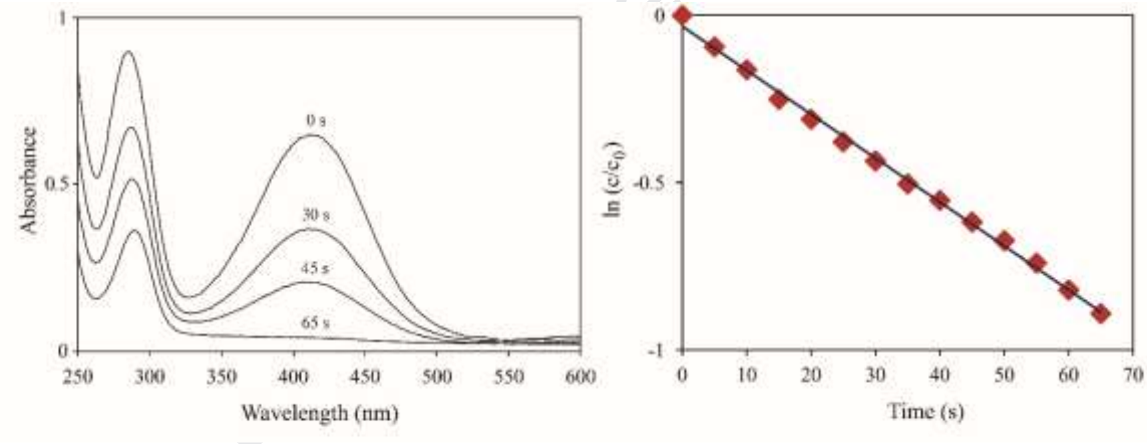


Fig. 6. UV-Vis spectrum of the product of 2-NA reduction in the presence of Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst (a) and linear dependence graph between $\ln(c/c_0)$ and time (b)

Table 4. Comparison of Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst with some reported catalysts in 2-NA reduction.

Entry	Catalyst	Amount of catalyst	Time	Ref.
1	SiO_2@Cu_xO@TiO_2	10 mg	150 s	[38]
2	MMT@Fe_3O_4@Cu MNPs	20 mg	6 min	[60]
3	Fe-Cu@MCC system	0.05g	8 min	[61]

4	Fe_3O_4@SiO_2@Cu-Ni-Fe-Cr LDH	0.01g	13 min	[62]
5	$NiFe_2O_4$@Cu NPs	0.15g	1 min	[63]
6	Pd NPs/RGO	6 mg	1.5 h	[64]
7	Ag/mNC nanocatalyst	5 mg	3 h	[65]
8	Fe_3O_4- Glu- Ag nanocatalyst	60 mg	12 min	[66]
9	Fe_3O_4@EDTA-Pd	20 mg	10 min	[67]
10	Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst	4 mg	65 s	Present study

3.3. Recyclability of Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst

Recyclability/recoverability is one of the significant properties of catalyst systems from economic, practical and sustainability aspects. Therefore, the reusability of Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst was tested in both *p*-$NO_2C_6H_4Br$ cyanation and 2-NA reduction. To reuse Pd/$CoFe_2O_4$/chitosan nanocatalyst, it was readily recovered using an external magnet after each catalytic test, rinsed with water and dried for further tests. The recyclability tests indicated that Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst successfully catalyzed both cyanation of *p*-$NO_2C_6H_4Br$ and reduction of 2-NA for five successive times. The SEM and TEM analyses of Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst after five cycles indicated that its particle size, shape and morphology were almost the same as that of the fresh catalyst (Fig. 7), confirming the excellent chemical stability of Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst.

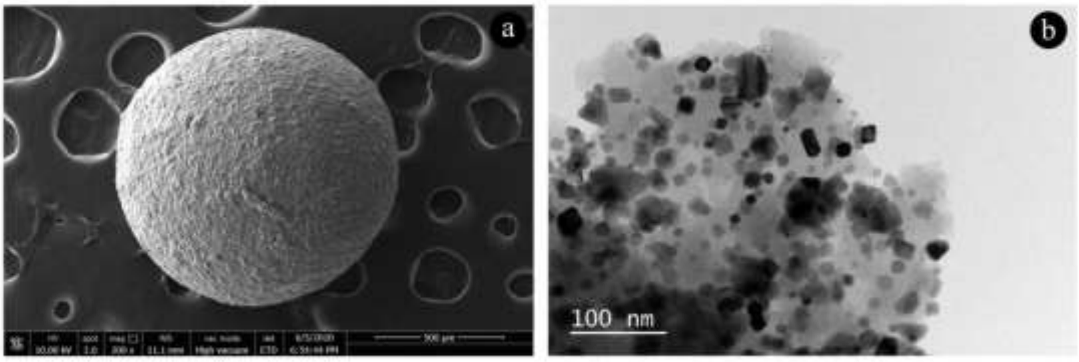


Fig. 7. SEM and TEM images of recycled Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst after the 5 runs.

4. Conclusion

In conclusion, a new heterogeneous palladium nanocatalyst system was successfully fabricated on $CoFe_2O_4$/chitosan beads as a stabilizer and characterized. Characterization studies showed that Pd NPs were immobilized on $CoFe_2O_4$/chitosan hybrid beads and their particle size was about 20 nm. The catalytic potential of Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst was then tested in the aryl halide cyanation and 2-NA reduction. Different benzonitriles were successfully generated with excellent yields using Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst. Additionally, Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst converted 2-NA to *o*-phenylenediamine within only 65 s. Furthermore, it was found that Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst can be reused up to five cycles in both reactions. To sum up, the designed catalytic system exhibited valuable characteristics such as facile recoverability, high stability, easy work-up, long life, and excellent catalytic activity within a short reaction time. Considering the unique properties of Pd/$CoFe_2O_4$/chitosan hybrid nanocatalyst, it can be utilized in the degradation of environmental pollutants such as organic dyes/nitroarenes and production of different benzonitriles.

Conflict of Interest: Authors declare no conflict of interest.

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Appendix A. Supplementary data

Contains information about the GC-MS spectra of synthesized benzonitriles.

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Research highlights:

- Preparation of palladium nanoparticles stabilized on $CoFe_2O_4$/chitosan hybrid beads.
- Catalytic reduction 2-nitroaniline in water at room temperature in a very short time.
- The catalyst shows excellent activity and generality in aryl halides cyanation.
- Nanocatalyst can be recovered and reused several times without any meaningful decreasing in the catalytic performance.

Declaration of interest: The authors declare no competing interest.