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FULL PAPER

Synthesis, characterization and catalytic performance of Pd(II) complex immobilized on Fe_3O_4@SiO_2 nanoparticles for the ligand-free cyanation of aryl halides using $K_4Fe(CN)_6$

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This work shows the preparation of a novel magnetic catalyst via immobilization of Pd(II)-*N*-benzyl-*N*-(4-bromophenyl)-5-amino-1*H*-tetrazole complex on the Fe_3O_4@SiO_2 nanoparticles (NPs). The application of Fe_3O_4@SiO_2 NPs supported Pd(II)-*N*-benzyl-*N*-(4-bromophenyl)-5-amino-1*H*-tetrazole complex [Fe_3O_4@SiO_2-BAT-Pd(II)] nanocatalyst is described for the cyanation of aryl iodides and bromides to the corresponding aryl nitriles using potassium hexacyanoferrate(II) [$K_4Fe(CN)_6$] as a non-toxic and economic cyanating agent under ligand- and additive-free conditions. Some aryl nitriles were efficiently synthesized from the corresponding aryl bromides and iodides in the presence of Fe_3O_4@SiO_2-BAT-Pd(II) nanocomplex. The core-shell nanocomplex demonstrated the superior catalytic performance for the synthesis of synthetically valuable aryl nitriles within good to excellent yields. This process eliminates the need to handle highly toxic metal cyanides, and it can be easily recovered and reused for six consecutive runs with no decreasing of its catalytic capability.

Highlights

- Preparation of Pd(II) complex immobilized on Fe_3O_4@SiO_2 nanoparticles [Fe_3O_4@SiO_2-BAT-Pd(II) nanocomplex].
- Characterization of Fe_3O_4@SiO_2-BAT-Pd(II) nanocomplex using XRD, FT-IR, EDS, VSM, TEM and FESEM analyses.
- Catalytic cyanation of the various aryl halides with $K_4Fe(CN)_6$ under ligand-free conditions.
- The nanocomplex can be recovered and isolated six times with no significant loss of its catalytic ability.

KEYWORDS
aryl nitriles, cyanation, Fe_3O_4@SiO_2-BAT-Pd(II), $K_4Fe(CN)_6$, palladium nanocomplex

1 | INTRODUCTION

Nitriles are a valuable molecular scaffold of organic materials. These compounds are versatile intermediates for the synthesis of organic moieties, such as esters, amines, amides, carboxylic acids, ketones and especially tetrazole-containing compounds as key synthetic precursors of various natural products, agricultural chemicals, pharmaceuticals, herbicides and dyes.[1–4] Besides, nitriles are not only important as biologically active substances in the synthesis of several drugs, but also are the industrial key solvent to carry out plentiful organic reactions.[4]

The synthesis of aryl nitriles attracted the attention of many researchers, because of their useful properties and potential applications. A number of groups have developed synthetic procedures in the literature for the preparation of the substituted aryl nitriles. Aryl nitriles can be conventionally synthesized via the reaction of aryl halides (Rosenmund–von Braun reaction) and aryl diazonium salts (Sandmeyer reaction) with a stoichiometric amount of CuCN, and also transition metal-catalyzed cyanation of aryl halides with toxic cyanide sources such as Me_3SiCN, $Zn(CN)_2$ and alkali-metal cyanides.[5–9] However, all of them have serious disadvantages, such as high reaction temperature (150–250°C), long reaction times, use of toxic, sensitive and metal cyanide sources, low yields, difficulty or little availability in preparing the starting reagents or catalysts, formation of high amounts of heavy metal wastes, and environmental pollutions that limit their applications.[10–14] Thus, the development of improved synthetic methods for the synthesis of these compounds to eliminate or reduce such limitations is much required.

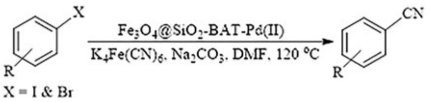
These limitations can be partially controlled with certain specific measures relevant to cyanide source. Later on, significant improvement for the cyanation reaction of aryl halides was obtained with introduction of a safe, inexpensive and non-flammable $K_4Fe(CN)_6$ reagent as cyanide source.[15–20] This reagent is non-toxic compared with former cyanide sources as which all cyanide groups of the iron center could be coupled with various aryl halides. For these reasons, $K_4Fe(CN)_6$ has received much interest as a safe cyanide source for the synthesis of aryl nitriles.[15,18–20]

Over the last years, various ligands (e.g. ethylenediamine and *N*,*N*′-dimethylethylenediamine) and homogeneous catalytic systems have been developed for the preparation of aryl nitriles using $K_4Fe(CN)_6$,[13,21–25] although difficulties and challenges in recovering and reusing the nanocatalysts limited their widespread application in industry. Therefore, the development of new, efficient and convenient techniques for the preparation of aryl nitriles under heterogeneous catalytic systems and ligand/additive-free conditions is still demanding in wide areas of research and industry.

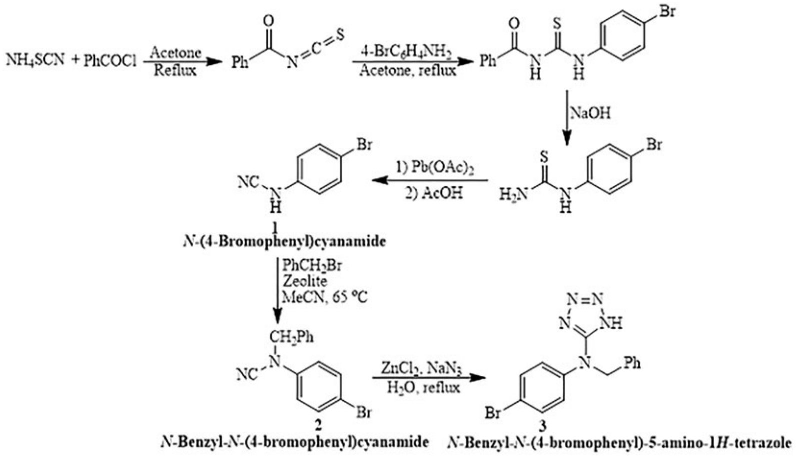
Thus far, due to the easy recovery, low toxicity, greater available catalytic surface and high catalytic activity, heterogeneous systems have been more and more developed to fabrication of nanostructures.[26–31] Among nanostructures, magnetic core-shell complexes are promising candidates because of their different applications in optical, medicinal, environmental, biological, material and chemical areas.[32–38] Further, core-shell magnetic nanoparticles (MNPs) can merge the properties of magnetic core and various functional shells to show many superior characteristics, such as chemical stability, good biocompatibility, low toxicity, large pore volumes, magnetic susceptibility, high surface areas, rigidity and controllable surface functionalization.[36,39–41]

Recently, the use of core-shell nanocomplexes as effective heterogeneous nanocatalysts has been rapidly increased in a widespread variety of organic transformations.[42] Most recently, our laboratory designed the synthesis of nanocomplexes using core-shell MNPs supported ionic liquids or copper and palladium complexes with various tetrazoles as nitrogen-rich heterocycles.[43–45] Thus, the synthesis and surface modification of MNPs has attracted an ever growing attention due to all these mentioned advantages in organocatalysis applications to propose new windows in an active research area.

Through this study, for the first time, we have designed an effective, heterogeneous and novel magnetic nanocomplex using *N*-benzyl-*N*-(4-bromophenyl)-5-amino-1*H*-tetrazole as a new ligand for the synthesis of aryl nitriles through cyanation of aryl iodides or bromides using $K_4Fe(CN)_6$ under ligand-free conditions (Scheme 1). The $Fe_3O_4@SiO_2$-BAT-Pd(II) catalyst is synthesized via immobilization of Pd(II)-*N*-benzyl-*N*-(4-bromophenyl)-5-amino-1*H*-tetrazole complex on the surface of $Fe_3O_4@SiO_2$ nanostructure. It is noteworthy that there is no report on the synthesis of magnetic nanocomplex-based aminotetrazoles. Therefore, this report can create a new approach to the production of magnetic nanocomplex-based aminotetrazole. The results show that the $Fe_3O_4@SiO_2$-BAT-Pd(II) catalyst has excellent catalytic activity in the cyanation of aryl halides. This procedure has advantages, such as short reaction times, high yields, simple methodology and work-up process, high catalytic activity, easy preparation, separation, stability and reusability of the catalyst.



SCHEME 1 Catalytic cyanation of aryl halides under ligand-free conditions



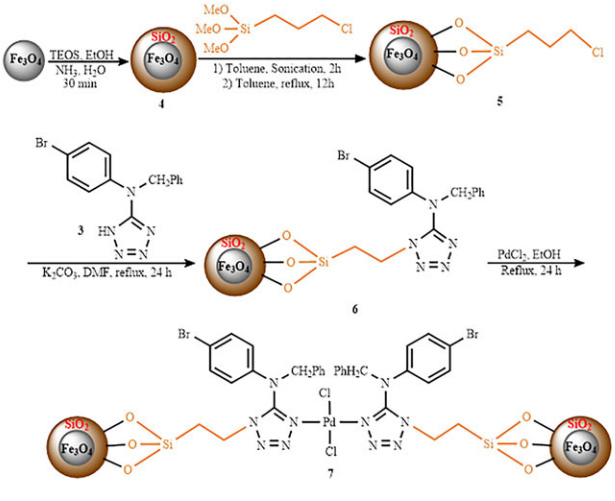
SCHEME 2 Synthesis of *N*-(4-bromophenyl) cyanamide (**1**), *N*-benzyl-*N*-(4-bromophenyl) cyanamide (**2**) and *N*-benzyl-*N*-(4-bromophenyl)-5-amino-1*H*-tetrazole (**3**)

2 | RESULTS AND DISCUSSION

2.1 | Preparation and characterization of the $Fe_3O_4@SiO_2$-BAT-Pd(II) nanocomplex

In continuation of our previous studies on the synthesis of arylcyanamides, *N*-benzyl-arylcyanamides and arylaminotetrazoles, herein, we were interested in designing a novel magnetic complex as which the *N*-benzyl-arylaminotetrazole was immobilized on the $Fe_3O_4@SiO_2$ NPs surface. In the present study, the *N*-(4-bromophenyl) cyanamide (**1**), *N*-benzyl-*N*-(4-bromophenyl) cyanamide (**2**) were prepared from the 4-bromoaniline according to Scheme 2. As shown in Scheme 2, for the first time we reported the synthesis of *N*-benzyl-*N*-(4-bromophenyl)-5-amino-1*H*-tetrazole (**3**) using $ZnCl_2$ in water under reflux conditions. In view of the present findings, the catalytic activity of Pd(II)-*N*-benzyl-*N*-(4-bromophenyl)-5-amino-1*H*-tetrazole complex immobilized on the $Fe_3O_4@SiO_2$ NPs was evaluated to the synthesis of aryl nitriles through the cyanation of aryl halides with $K_4Fe(CN)_6$ at 120°C. Thus, aryl nitriles were successfully prepared in the presence of the $Fe_3O_4@SiO_2$-BAT-Pd(II) nanocomplex using $K_4Fe(CN)_6$ as an available and inexpensive cyanide source without using ligand or additive that lead to good atom efficiency.

The synthetic procedure of the $Fe_3O_4@SiO_2$-BAT-Pd(II) complex is schematically shown in Scheme 3. The first step involves the fabrication of $Fe_3O_4@SiO_2$ NPs (**4**) using coating a non-porous SiO_2 shell around superparamagnetic Fe_3O_4 NPs through self-assembly, condensation and hydrolysis of tetraethylorthosilicate



SCHEME 3 Preparation of $Fe_3O_4@SiO_2$-BAT-Pd(II) (**7**)

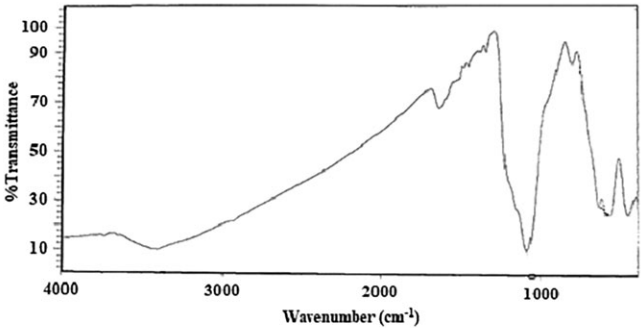


FIGURE 1 Fourier transform-infrared (FT-IR) spectrum of the $Fe_3O_4@SiO_2$-BAT-Pd(II) (**7**) nanocomplex

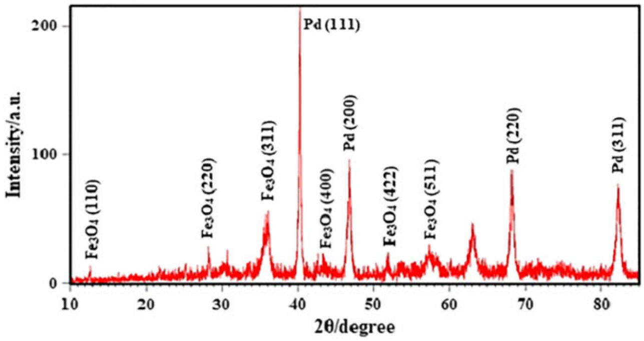


FIGURE 2 X-ray diffraction analysis (XRD) pattern of the $Fe_3O_4@SiO_2$-BAT-Pd(II) (**7**) nanocomplex

(TEOS).[9] In the next step, further modification was performed using grafting of the 3-chloropropyltriethoxysilane with $Fe_3O_4@SiO_2$. Then, grafting of $Fe_3O_4@SiO_2@(CH_2)_3Cl$ (**5**) with *N*-benzyl-*N*-(4-bromophenyl)-5-amino-1*H*-tetrazole (**3**) via a nucleophilic substitution process, and finally $Fe_3O_4@SiO_2$-BAT-Pd(II) (**7**) was prepared using incorporation of $Fe_3O_4@SiO_2@(CH_2)$-*N*-benzyl-*N*-(4-bromophenyl)-5-amino-1*H*-tetrazole (**6**) with palladium ions under reflux conditions. To date, this is the only report wherein a magnetic complex-based *N*-benzyl-*N*-arylaminotetrazole was used in catalysis.

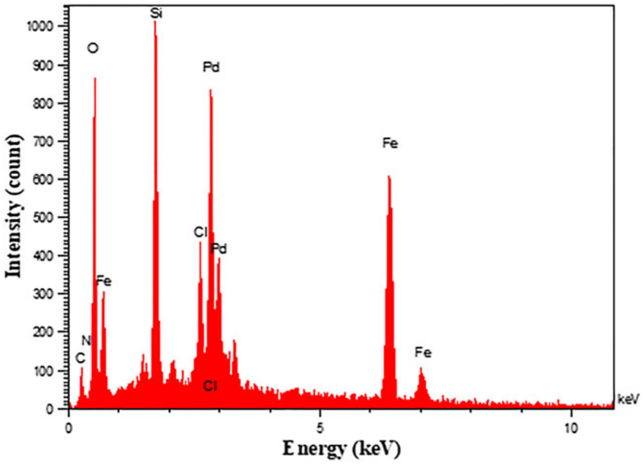


FIGURE 3 Energy-dispersive X-ray spectroscopy (EDS) spectrum of the $Fe_3O_4@SiO_2$-BAT-Pd(II) (**7**) nanocomplex

The $Fe_3O_4@SiO_2$-BAT-Pd(II) (**7**) catalyst then was identified by using field emission scanning electron microscopy (FESEM), X-ray diffraction analysis (XRD), Fourier transform-infrared (FT-IR), vibrating-sample magnetometer (VSM), transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS) analyses.

The FT-IR spectrum of as-prepared complex is shown in Figure 1. The peaks at about 3550–1600 cm^{-1} are assigned to the O-H and N-H groups of the Fe_3O_4 MNPs. Additionally, the peaks at 575 and 632 cm^{-1} are due to

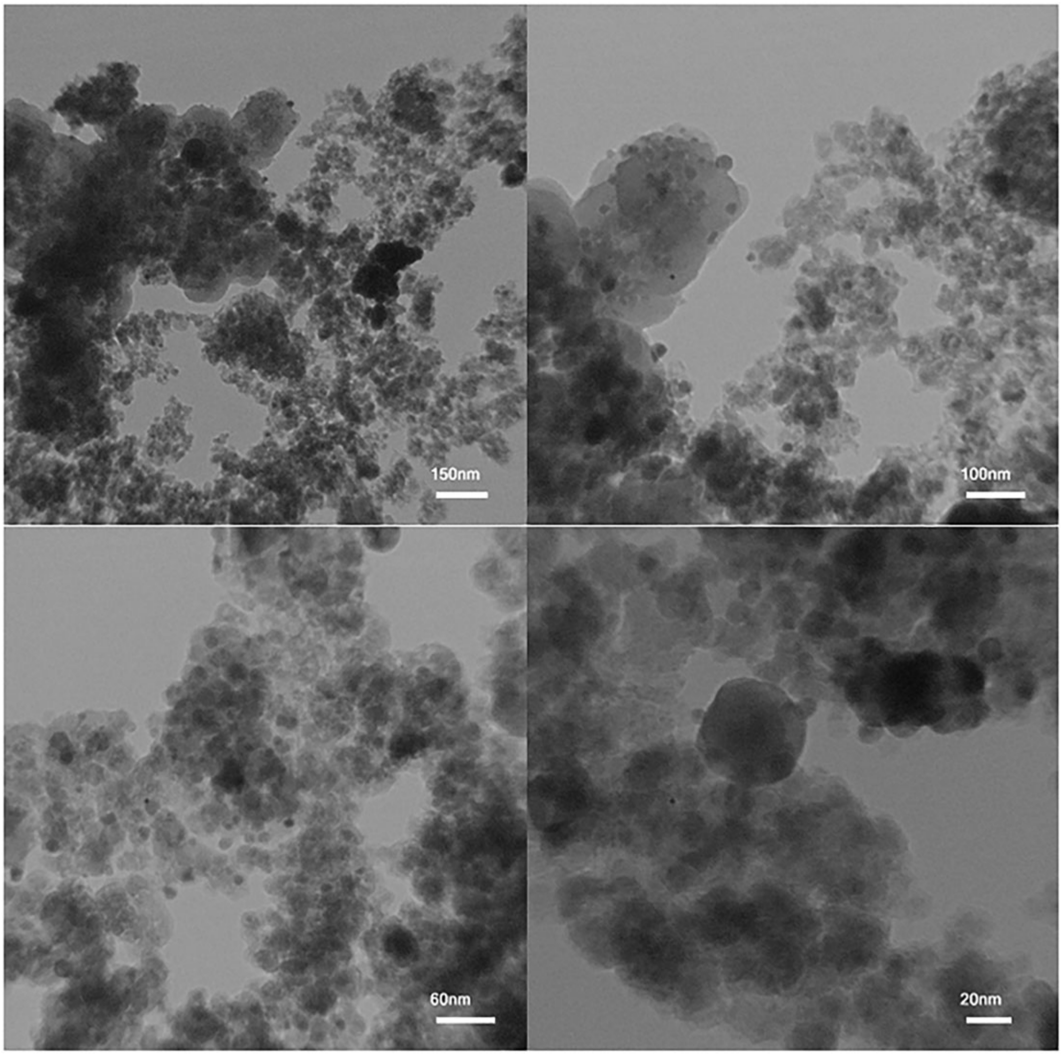


FIGURE 4 Transmission electron microscopy (TEM) images of the $Fe_3O_4@SiO_2$-BAT-Pd(II) (**7**) nanocomplex

the Fe-O stretching vibration in the Fe_3O_4 MNPs. The fabrication of $Fe_3O_4@SiO_2$ core-shell was confirmed by the peaks that appeared at 454, 800 and 1083 cm^{-1}, which are attributed to Si-O-Si bending, Si-O bending, and Si-O-Si stretching, respectively. Also, the peaks at 1353 and 1644 cm^{-1} correspond to the N=N and C=N stretching bands of tetrazole ligand, indicating the grafting of ligand on the surface of $Fe_3O_4@SiO_2-CH_2Cl$.

For further convenience, the XRD pattern of $Fe_3O_4@SiO_2$-BAT-Pd(II) (**7**) was performed to identify the crystallographic structure of magnetite complex (Figure 2). As shown in Figure 2, seven sharp diffraction peaks located at $2\theta = 12.60°$, 28.20°, 36.00°, 43.20°, 51.80°, 57.20° and 63.1° were assigned to (110), (220), (311), (400), (422), (511) and (440) crystal planes of the cubic spinel structures of MNPs. The diffraction peaks at $2\theta = 40.2°$, 47.0°, 68.1° and 82.2° can be indexed to (111), (200), (220) and (311) Bragg's reflections of face-centered Pd. The particle's size can be found by applying Sherrer's equation, where the average particle size is found to be 27 nm.

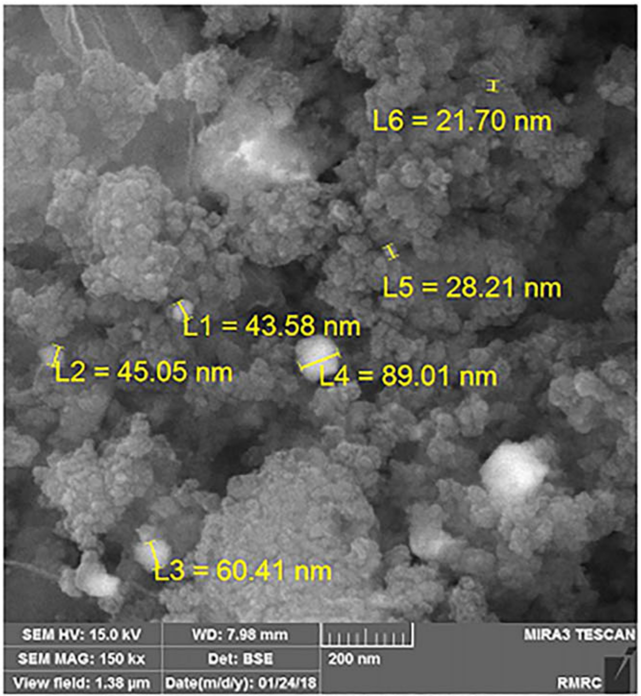


FIGURE 5 Field emission scanning electron microscopy (FESEM) images of the $Fe_3O_4@SiO_2$-BAT-Pd(II) (**7**) nanocomplex

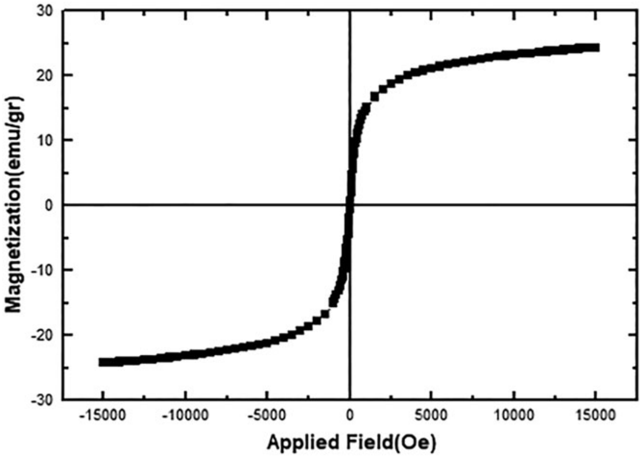
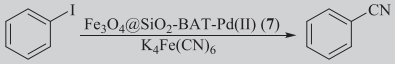


FIGURE 6 Magnetization curve for the $Fe_3O_4@SiO_2$-BAT-Pd(II) (**7**) nanocomplex

TABLE 1 Optimization of the reaction conditions for the cyanation of phenyl iodide with $K_4Fe(CN)_6$[a]



Entry	$Fe_3O_4@SiO_2$-BAT-Pd(II) (7) (mg)	Solvent	Base	Yield[b] (%)
1	0.0	DMF	Na_2CO_3	0.0
2	0.05	DMF	Na_2CO_3	89
3	0.05	DMSO	Na_2CO_3	86
4	0.05	Toluene	Na_2CO_3	16
5	0.05	H_2O	Na_2CO_3	15
6	0.05	NMP	Na_2CO_3	28
7	0.05	DMF	K_2CO_3	79
8	0.05	DMF	Et_3N	19
9	0.05	DMF	NaF	24
10	0.05	DMF	KOAc	77
11	0.035	DMF	Na_2CO_3	63
12	0.07	DMF	Na_2CO_3	89

[a] Reaction conditions: phenyl iodide (1.0 mmol), $K_4Fe(CN)_6$ (0.17 mmol), base (1.0 mmol), DMF (7.0 mL), 120°C, 5 hr.

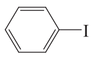
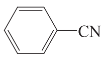
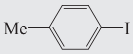
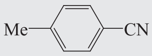
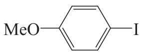
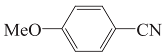
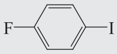
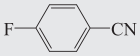
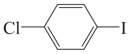
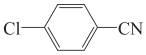
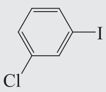
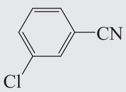
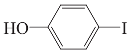
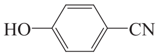
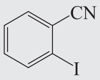
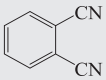
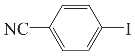
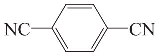
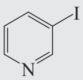
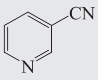
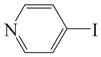
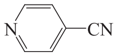
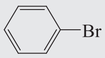
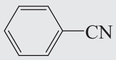
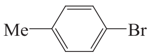
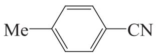
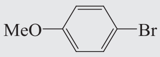
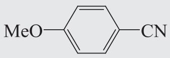
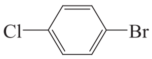
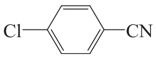
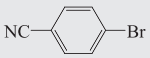
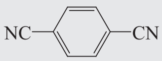
[b] Isolated yield. DMF, dimethylformamide; NMP, N-Methyl-2-pyrrolidone.

Besides, the EDS spectrum of Fe_3O_4@SiO_2-BAT-Pd(II) (**7**) catalyst clearly shows the presence of corresponding elements in its chemical structure (Figure 3). In the EDS analysis of Fe_3O_4@SiO_2-BAT-Pd(II) (**7**), iron Fe, O, Si, N, Cl, C and Pd peaks were illustrated, indicating that the Pd(II)-*N*-benzyl-*N*-(4-bromophenyl)-5-amino-1*H*-tetrazole complex grafted on the Fe_3O_4@SiO_2 NPs surface (Figure 3). The aforementioned results proved the successful synthesis of Fe_3O_4@SiO_2-benzylaminotet-Pd(II) magnetic complex.

TABLE 2 Cyanation of aryl halides with $K_4Fe(CN)_6$ in the presence of Fe_3O_4@SiO_2-BAT-Pd(II) (**7**) nanocomplex[a]

$$\text{ArX} \xrightarrow[\text{K}_4\text{Fe(CN)}_6\text{, Na}_2\text{CO}_3\text{, DMF, 120 °C}]{\text{Fe}_3\text{O}_4\text{@SiO}_2\text{-BAT-Pd(II) (7)}} \text{ArCN}$$

X = I & Br

Entry	ArX	Product	Time (hr)	Yield[b] (%)
1			5	89
2			7	90
3			7	90
4			5	95
5			5	93
6			6	91
7			5	91
8			5	93
9			5	92
10			5	94
11			5	94
12			7	89
13			7	91
14			7	90
15			7	91
16			7	92

[a] Reaction conditions: Fe_3O_4@SiO_2-BAT-Pd(II) (**7**) (0.05 g), aryl halide (1.0 mmol), $K_4Fe(CN)_6$ (0.17 mmol), Na_2CO_3 (1.0 mmol), DMF (7.0 mL), 120°C.

[b] Isolated yield.

The surface morphology, size and structure of the nanocomplex was investigated by TEM and FESEM images (Figures 4 and 5, respectively). As revealed in Figure 4, the TEM analysis of the complex confirmed that Fe_3O_4@SiO_2 MNPs with the spherical shape and the nanometer size particles were prepared with low tendency to agglomeration. The FESEM images of as-prepared nanocomplex are shown in Figure 5. It can also be concluded that the surface of Fe_3O_4@SiO_2 nanostructure is covered with Pd(II)-*N*-benzyl-*N*-(4-bromophenyl)-5-amino-1*H*-tetrazole complex (Figure 5). Based on the aforesaid analyses, the structure of the novel fabricated catalyst was entirely confirmed.

The hysteresis loop of Fe_3O_4@SiO_2-BAT-Pd(II) (**7**) nanocomplex was achieved in the applied magnetic field at room temperature, with the field sweeping from −15 000 to +15 000 Oe using a SQUID magnetometer (Figure 6). As shown in Figure 6, the saturation magnetization (M_s) values of the Fe_3O_4 and Fe_3O_4@SiO_2-BAT-Pd(II) (**7**) nanocomplex were measured to be about 60.0

$$\text{ArI} \xrightarrow[\text{K}_4\text{Fe(CN)}_6\text{, Na}_2\text{CO}_3\text{, DMAc, 120 °C, 1-8 h}]{\text{Pd(OAC)}_2\text{, N}_2\text{ atm}} \text{ArCN} \qquad \text{(Eq. 1)}$$

$$\text{ArI} \xrightarrow[\text{K}_4\text{Fe(CN)}_6\text{, KF, DMF, 120 °C, 15 h}]{\text{Cu(I)-HAP, DMEDA}} \text{ArCN} \qquad \text{(Eq. 2)}$$

$$\text{ArX} \xrightarrow[\text{K}_4\text{Fe(CN)}_6\text{, Na}_2\text{CO}_3\text{, NMP,120-140 °C, 16 h}]{\text{Pd(OAC)}_2\text{, dppf, inert conditions}} \text{ArCN} \qquad \text{(Eq. 3)}$$

$$\text{ArI} \xrightarrow[\text{K}_4\text{Fe(CN)}_6\text{, Cs}_2\text{CO}_3\text{, DMF, 130 °C, 10 h}]{\text{CuI, Ligand, N}_2\text{ atm}} \text{ArCN} \qquad \text{(Eq. 4)}$$

Ligand: 1,2-bis(5-tetrazoyl)benzene

$$\text{ArX} \xrightarrow[\text{DMF, 120 °C, 45 h}]{\text{CuCN, L-proline}} \text{ArCN} \qquad \text{(Eq. 5)}$$

$$\text{ArI} \xrightarrow[\text{HCON(Me)}_2\text{, DMF, 140 °C, 48 h}]{\text{Cu(NO}_3)_2\text{.3H}_2\text{O, HOAc, TBHP}} \text{ArCN} \qquad \text{(Eq. 6)}$$

$$\text{ArBr} \xrightarrow[\text{K}_4\text{Fe(CN)}_6\text{, K}_2\text{CO}_3\text{, 100 °C, 18 h}]{\text{Pd complex, dioxane/H}_2\text{O}} \text{ArCN} \qquad \text{(Eq. 7)}$$

$$\text{ArBr} \xrightarrow[\text{K}_4\text{Fe(CN)}_6\text{, 85 °C, 4-16 h}]{\text{Pd(PPh}_3)_4\text{, DBU, t-BuOH/H}_2\text{O}} \text{ArCN} \qquad \text{(Eq. 8)}$$

$$\text{ArBr} \xrightarrow[\text{K}_4\text{Fe(CN)}_6\text{, Cs}_2\text{CO}_3\text{, DMF, 130 °C, 8 h}]{\text{CuI, KI, ligand, N}_2\text{ atm}} \text{ArCN} \qquad \text{(Eq. 9)}$$

Ligand: 3,3'-(1,4-phenylene)bis-(2-imino-2,3-dihydrobenzo[*d*]-oxazol-5ol)

$$\text{ArBr} \xrightarrow[\text{K}_4\text{Fe(CN)}_6\text{, KF, DMF, 130 °C, 14 h}]{\text{ZnO-Pd NPs}} \text{ArCN} \qquad \text{(Eq. 10)}$$

$$\text{ArI} \xrightarrow[\text{K}_4\text{Fe(CN)}_6\text{, K}_2\text{CO}_3\text{, DMF, 120 °C, 10-15 h}]{\text{Pd/CuO NPs, DMEDA}} \text{ArCN} \qquad \text{(Eq. 11)}$$

$$\text{ArX} \xrightarrow[\text{K}_4\text{Fe(CN)}_6\text{, Na}_2\text{CO}_3\text{, DMF, 120 °C, 5-7 h}]{\text{Fe}_3\text{O}_4\text{@SiO}_2\text{-benzylaminotet-Pd(II)}} \text{ArCN} \qquad \text{(Eq. 12)}$$

SCHEME 4 The cyanation of aryl halides under different reaction conditions and 25.0 emu g^{-1}, respectively. The M_s of the nanocomplex is smaller than Fe_3O_4 NPs owing to surface modification of the Fe_3O_4 core with SiO_2 shell and tetrazole ligand. These results clearly verified the synthesis of Fe_3O_4@SiO_2-BAT-Pd(II) as a nanomagnetic complex.

2.2 | Preparation of aryl nitriles using Fe_3O_4@SiO_2-BAT-Pd(II) (7) nanocomplex

After characterization of novel magnetic catalyst, the catalytic activity of Fe_3O_4@SiO_2-BAT-Pd(II) (**7**) nanocomplex was evaluated for the synthesis of aryl nitriles via cyanation reaction of aryl iodides and bromides with $K_4Fe(CN)_6$ as a suitable cyanide source. Initial studies were tested in order to examine the reaction conditions for the cyanation of phenyl iodide with $K_4Fe(CN)_6$ in the presence of the Fe_3O_4@SiO_2-BAT-Pd(II) (**7**) catalyst as a model process (Table 1). The optimization of the effect of catalyst amount was assessed. As shown in Table 1, the reaction cannot be carried out in the absence of Fe_3O_4@SiO_2-BAT-Pd(II) (**7**) catalyst (entry 1). However, addition of the nanocatalyst to the mixture has quickly increased the synthesis of benzonitrile in higher yields. The effect of base and solvent on the cyanation of phenyl iodide was also investigated. Dimethylformamide (DMF) as solvent and Na_2CO_3 (sodium carbonate) as base are clearly the best choices to give an excellent yield of product (Table 1, entry 2). The optimum amount of Fe_3O_4@SiO_2-BAT-Pd (II) (**7**) was obtained as 0.05 g (Table 1, entry 2). The best result can be achieved with iodobenzene (1.0 mmol), $K_4Fe(CN)_6$ (0.17 mmol) and Na_2CO_3 (1.0 mmol) in the presence of 0.05 g of Fe_3O_4@SiO_2-BAT-Pd(II) (**7**) as an effective catalyst in DMF (Table 1, entry 2). Larger amounts of catalyst did not improve the reaction yield (Table 1, entry 12), while smaller amounts of catalyst clearly decrease the reaction yield (Table 1, entry 11).

Upon optimization of reaction conditions, a series of aryl halides possessing electron-withdrawing or electron-donating substituents were subsequently subjected to ligand-free cyanation reaction, and the results were shown in Table 2. A widespread variety of aryl bromides and aryl iodides were transformed into the corresponding substituted aryl nitriles. It was observed that aryl halides bearing electron-donating substituents gave corresponding aryl nitriles in similar excellent yields compared with electron-withdrawing substituents. Activated and non-activated aryl halides were reacted under

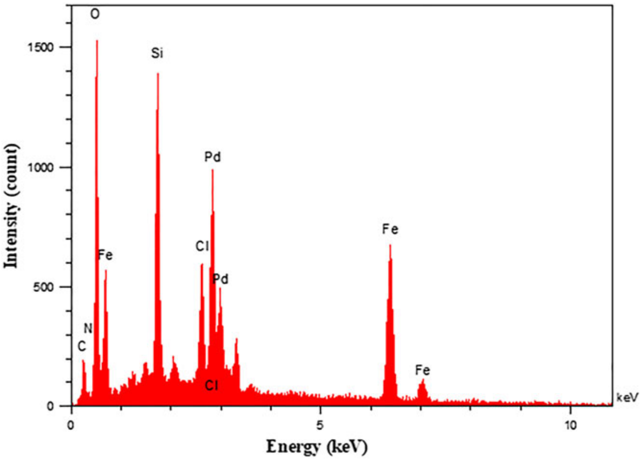


FIGURE 8 Energy-dispersive X-ray spectroscopy (EDS) spectrum of reused Fe_3O_4@SiO_2-BAT-Pd(II) catalyst after sixth recycle

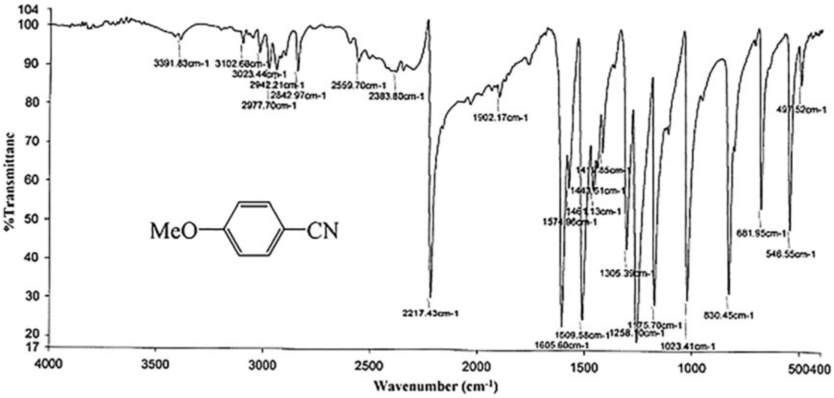


FIGURE 7 Fourier transform-infrared (FT-IR) spectrum of 4-methoxybenzonitrile

TABLE 3 Reusability and recoverability of Fe_3O_4@SiO_2-BAT-Pd(II) nanocomplex for cyanation of phenyl iodide with $K_4Fe(CN)_6$[a]

Recycle	First	Second	Third	Fourth	Fifth	Sixth
Yield[b](%)	89	89	88	87	86	85

[a] Reaction conditions: Fe_3O_4@SiO_2-BAT-Pd(II) (0.05 g), phenyl iodide (1.0 mmol), $K_4Fe(CN)_6$ (0.17 mmol), Na_2CO_3 (1.0 mmol), DMF (7.0 mL), at 120°C, 5hr.

[b] Isolated yield.

ligand- and additive-free conditions. In addition, apart from aryl halides, we tested heteroaromatic iodides (Table 2, entries 10 and 11). All products can be successfully obtained in high yields and characterized by FT-IR and NMR spectra.

Scheme 4 shows some reported methods in the literature [equations (1–11)][17,20,46–54] for the cyanation of aryl halides with $K_4Fe(CN)_6$, and also presents synthetic methods (equation 12) under different reaction conditions in order to further understand the efficiency and advantages of our method. The following items can be inferred from the literature about different procedures for the cyanation of aryl halides with different cyanide sources:

- harsh reaction conditions and tedious work-up;
- usage of toxic, expensive and explosive reagents;
- formation of by-products and impurities within long reaction times;
- usage of ligand (difficulties in availability and preparation of substrate);
- the use of homogeneous catalysts that cannot be easily recycled and recovered; and
- column chromatography was required for the purification of the aryl nitriles.

Among all the reported methods for the preparation of aryl nitriles in the literature,[17,20,46–54] our method (equation 12) was completely the best type of protocol due to preparation of an effective, novel and magnetically separable heterogeneous catalyst, avoidance of the toxic ligands, wide substrate scope and generality, simpler work-up, higher yields, shorter reaction time and convenient reaction system, which make it an attractive and beneficial strategy for the cyanation of aryl halides. Besides, in contrast with other nanocatalysts, Fe_3O_4@SiO_2-BAT-Pd(II) (**7**) can be easily recovered from the reaction using an external magnet and reused several times. None of the above-mentioned disadvantages was also observed.

All products were characterized by ^{1}H-NMR, ^{13}C-NMR and FT-IR spectra, and melting points. Additionally, the physical data of the known aryl nitriles were identical with those reported in the literature.[17,20,46–54] In FT-IR spectra, the appearance of one absorption peak of a CN stretching band of the nitriles in the range of 2225–2360 cm^{-1} can clearly confirm the preparation of the products (Figure 7).

3 | CATALYST REUSABILITY

One of the most industrial applications of heterogeneous catalytic systems is reusability and recyclability of nanocatalysts. For this goal, the catalytic capability of the recycled Fe_3O_4@SiO_2-BAT-Pd(II) was tested. As shown in Table 3, the cyanation of phenyl iodide with $K_4Fe(CN)_6$ was monitored to investigate the reusability of

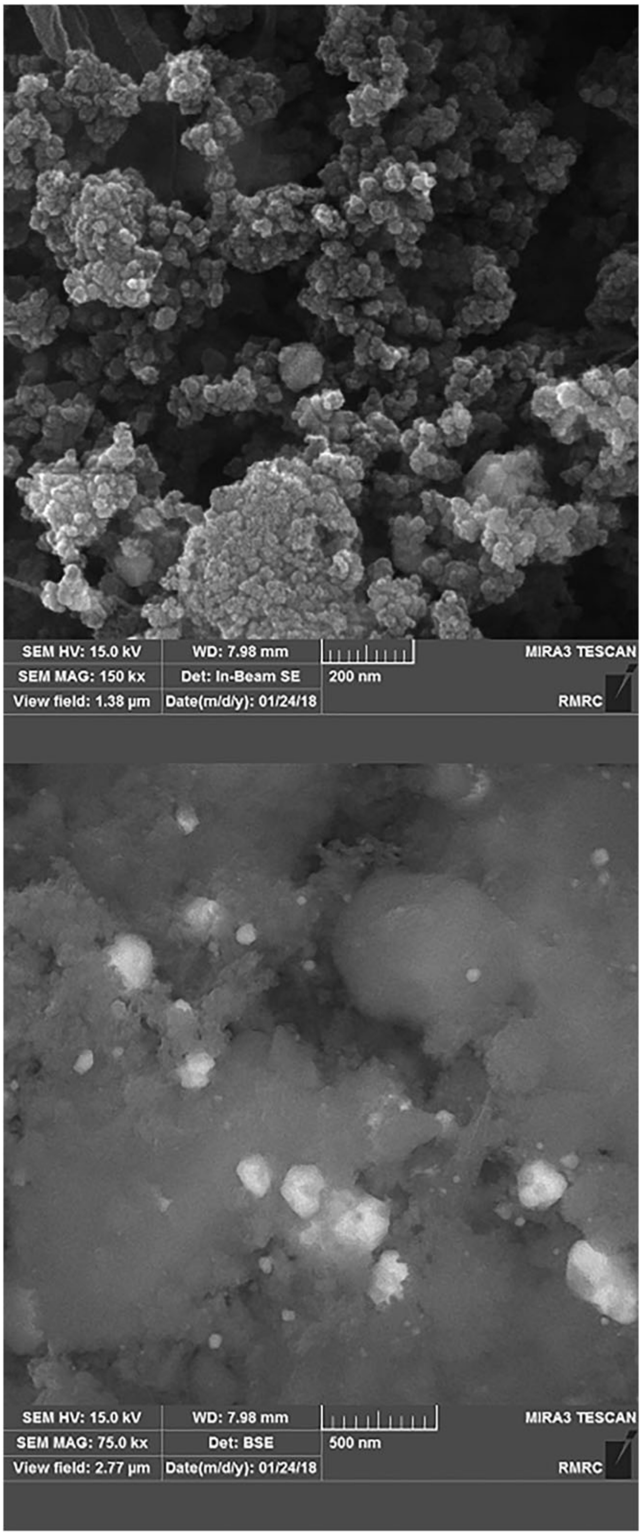


FIGURE 9 Field emission scanning electron microscopy (FESEM) images of recovered Fe_3O_4@SiO_2-BAT-Pd(II) catalyst after sixth recycle

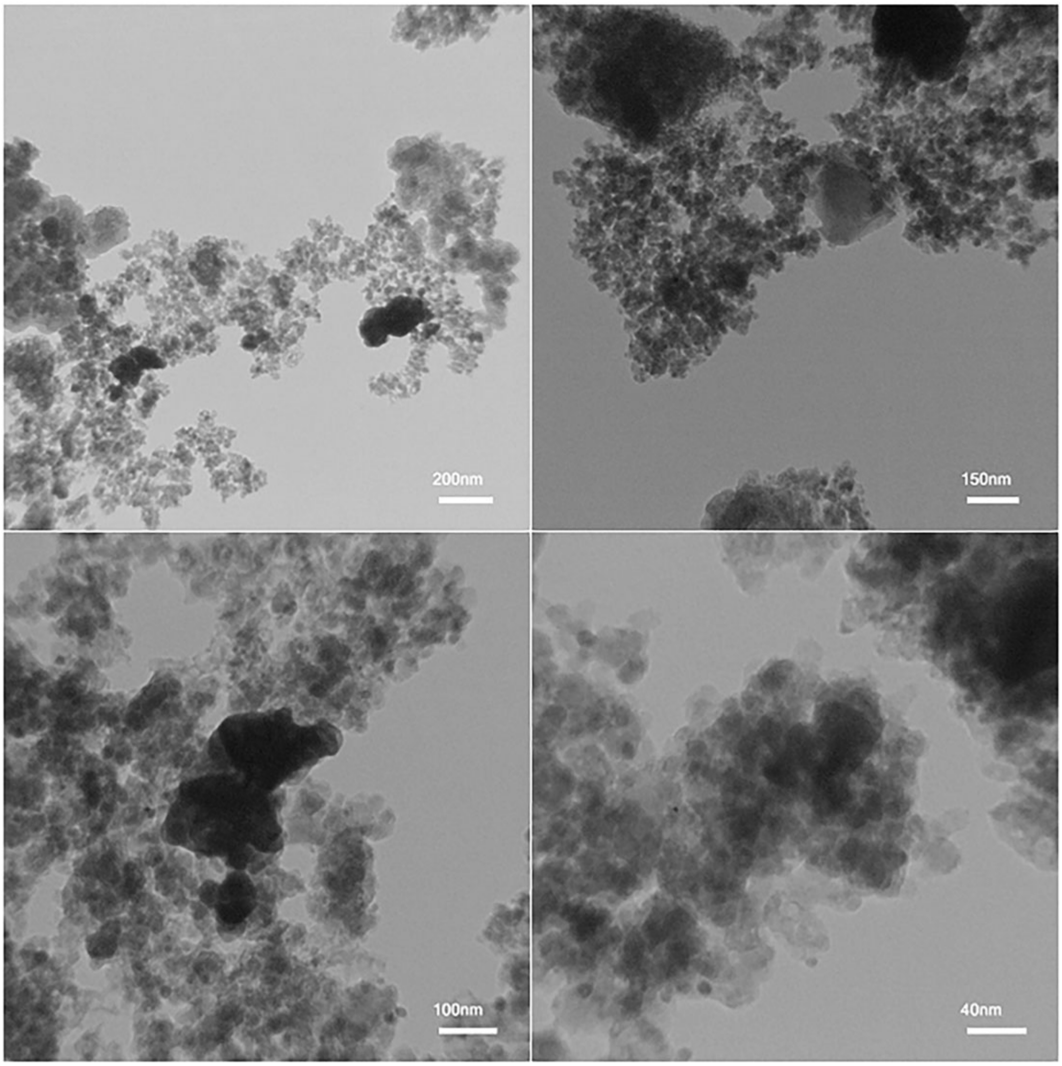


FIGURE 10 Transmission electron microscopy (TEM) images of reused Fe_3O_4@SiO_2-BAT-Pd(II) catalyst after sixth recycle

Fe_3O_4@SiO_2-BAT-Pd(II) catalyst under optimized conditions. When the cyanation reaction was completed, Fe_3O_4@SiO_2-BAT-Pd(II) could be easily recovered and isolated after every run by using magnetic decantation followed by washing with water and ethanol, then could be dried and finally reused for the consecutive run (Table 3). The Pd(II) complex was recycled for six consecutive runs with no decreasing of its catalytic capability. After the sixth run, the structure stability and morphology of recycled Fe_3O_4@SiO_2-benzylaminotet-Pd(II) was characterized by EDS, FESEM and TEM (Figures 8–10). However, some core-shell NP aggregations were observed.

4 | CONCLUSIONS

In the present work, we reported successful synthesis of an effective and novel magnetic catalyst composed of a Fe_3O_4 NPs core, SiO_2 shell and a Pd(II)-*N*-benzyl-*N*-(4-bromophenyl)-5-amino-1*H*-tetrazole complex. So far there has been no report about *N*-benzyl-arylaminotetrazole stabilized on the Fe_3O_4@SiO_2 MNPs surface. A beneficial series of analytical techniques was utilized to characterize a novel magnetic catalyst. The resulting Fe_3O_4@SiO_2-BAT-Pd(II) nanocomplex was utilized as an effective heterogeneous catalyst for the cyanation of aryl iodides and bromides to the corresponding aryl nitriles by using $K_4Fe(CN)_6$ as a cyanating agent under additive/ligand-free conditions. Compared with conventional methods, the advantages of this novel protocol are simple procedure, the use of environmentally benign and safe cyanide source, high yields of the products, high activity and recovery of the catalyst, and the elimination of ligand. Furthermore, the nanocomplex can be easily recovered and isolated from the reaction mixture using a magnetic decantation for at least six consecutive runs with no noticeable decreasing of its catalytic capability.

5 | EXPERIMENTAL

5.1 | Instruments and reagents

All materials, reagents and solvents of commercial grade were from Merck (Germany) and Sigma-Aldrich (USA). All materials are used in the current work without further purification. Structural confirmation of the aryl nitriles was performed using FT-IR, ^{1}H-NMR and ^{13}C-NMR spectra. The purity determination of the substrates and reaction monitoring were accomplished by thin-layer chromatography (TLC) on silica gel PolyGram SILG/UV254 plates. The NMR spectra were recorded on a Bruker (Avance DRX-400 MHz) spectrometer. The phase composition of nanocomplex was investigated by XRD (Philips type PW 1373 goniometer). The X-ray wavelength is Cu Kα radiation = 0.15406 nm, and the scanning speed was 2° per min in the 2θ range (10–80). Elemental analysis of Fe_3O_4@SiO_2-BAT-Pd(II) was measured using EDS performed in FESEM. The FT-IR (KBr) spectrum of the samples was measured using a Nicolet 370 FT/IR spectrometer (Thermo Nicolet, USA). The morphology and particle dispersion of Pd nanocomplex was investigated by TEM (Philips EM208) at an accelerating voltage of 90 kV and FESEM (Hitachi S-4700). VSM measurements were recorded using a SQUID magnetometer at 298 K (Quantum Design MPMS XL).

6 | SYNTHESIS OF *N*-(4-BROMOPHENYL)CYANAMIDE

N-benzyl-N-(4-bromophenyl) cyanamide was prepared according to the literature.[55]

6.1 | Synthesis of *N*-benzyl-*N*-(4-bromophenyl)-5-amino-1*H*-tetrazole

A mixture of *N*-benzyl-*N*-(4-bromophenyl) cyanamide (2.0 mmol), $ZnBr_2$ (2.0 mmol), sodium azide (3.0 mmol) in H_2O (15 mL) was stirred under reflux conditions for 24 hr. After completion of the reaction (monitored by TLC), the solid residue was filtered, washed with water treated with 4.0 mL of HCl (3 M), and the resulting product was recrystallized using aq. EtOH.

6.2 | Preparation of Fe_3O_4@SiO_2 core-shell NPs

The silica-coated Fe_3O_4 NPs were obtained via the reported routes in the literature.[9,41] Firstly, 1.0 g of the Fe_3O_4 NPs, 3.0 mL of NH_3 (25%), 25.0 mL of deionized water and 85.0 mL of ethanol (98%) were mechanically dispersed using sonication for 25 min. Then, 3.0 mL of TEOS as coating agent was added to the reaction solution, and finally the above mixture was refluxed to afford core-shell NPs.

6.3 | Preparation of Fe_3O_4@SiO_2@$(CH_2)_3Cl$

In a 250-mL flask, 3.0 g of Fe_3O_4@SiO_2, 80.0 mL of dry toluene and 10.0 mmol of (3-chloropropyl) trimethoxysilane were stirred and refluxed under nitrogen for 12 hr. The as-prepared Fe_3O_4@SiO_2@$(CH_2)_3Cl$ was cooled at room temperature then separated using a magnet, and washed several times with deionized water and dry toluene. The resulting product was dried at 75°C for 7 hr in a vacuum.

6.4 | Preparation of Fe_3O_4@SiO_2@$(CH_2)_3$-benzylaminotet

In the next step, further modification was performed using the immobilization of *N*-benzyl-*N*-(4-bromophenyl)-5-amino-1*H*-tetrazole on the as-prepared Fe_3O_4@SiO_2@$(CH_2)_3Cl$ via a nucleophilic substitution reaction. *N*-Benzyl-*N*-(4-bromophenyl)-5-amino-1*H*-tetrazole (5.0 mmol) and K_2CO_3 (5.0 mmol) in DMF (55.0 mL) were added to the Fe_3O_4@SiO_2@$(CH_2)_3Cl$ (2.0 g), and then the above-mentioned mixture was mixed and refluxed for 24 hr. Next, the resulting solid was collected by external magnet, washed with DMF and distilled water, and then dried.

6.5 | Preparation of Fe_3O_4@SiO_2-BAT-Pd(II)

Finally, a solution of $PdCl_2$ (0.4 g) was added to Fe_3O_4@SiO_2@$(CH_2)_3$-benzylaminotet (1.0 g) in 50.0 mL of ethanol, and the reaction mixture was stirred under reflux conditions for 24 hr. Finally, with similar steps of separating, washing and drying, the resulting Fe_3O_4@SiO_2-BAT-Pd(II) as a novel and magnetically heterogeneous catalyst was obtained.

6.6 | General protocol for the synthesis of aryl nitriles

Typically, a mixture of Fe_3O_4@SiO_2-BAT-Pd(II) (0.05 g), aryl halides (1.0 mmol), Na_2CO_3 (1.0 mmol) and $K_4Fe(CN)_6$ (0.17 mmol) in DMF (7.0 mL) was stirred at 120°C for the appropriate time. After consumption of aryl halides (as monitored by TLC), the reaction mixture was cooled and the core-shell nanocatalyst could be recovered using an external magnetic separator. Then, H_2O and ethyl acetate (EtOAc) were added to the reaction mixture while shaking vigorously. The organic layer was extracted, dried over $MgSO_4$, filtered and then evaporated to give the products in excellent yields. The resulting products were purified by using recrystallization. All the physical and spectral data of the synthesized nitriles were found to be identical in comparison with those reported in the literature.[17,20,46–54]

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