### Journal of Catalysis 365 (2018) 204-212

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

## In *situ* immobilized palladium nanoparticles on surface of polymethyldopa coated-magnetic nanoparticles (Fe<sub>3</sub>O<sub>4</sub>@PMDA/Pd): A magnetically recyclable nanocatalyst for cyanation of aryl halides with $K_4$ [Fe(CN)<sub>6</sub>]



JOURNAL OF CATALYSIS

### Hojat Veisi\*, Saba Hemmati, Parisa Safarimehr

Department of Chemistry, Payame Noor University, Tehran, Iran

### ARTICLE INFO

Article history: Received 30 April 2018 Revised 15 June 2018 Accepted 2 July 2018

Keywords: Cyanation Poly-methyldopa Magnetic Palladium Core/shell Aryl nitrile

### ABSTRACT

Poly-methyldopa (PMDP)-coated Fe<sub>3</sub>O<sub>4</sub> nanoparticles (Fe<sub>3</sub>O<sub>4</sub>@PMDP) have been synthesized through a simple and green procedure. In the present study, for the first time, Pd nanoparticles were successfully deposited using Fe<sub>3</sub>O<sub>4</sub>@PMDP as a core-shell magnetic coordinator and stabilizer agent. In this protocol, Pd ions were adsorbed on surfaces of Fe<sub>3</sub>O<sub>4</sub>@PMDP through immersion of the PMDP-coated Fe<sub>3</sub>O<sub>4</sub> nanoparticles into a palladium plating bath. Next, they were reduced *in situ* to palladium nanoparticles using PMDP's *N*-containing groups and reducing ability. The structure, morphology and physicochemical properties of the synthesized nanoparticles were characterized by different analytical techniques such as energy-dispersive X-ray spectroscopy (EDS), field emission scanning electron microscope (FESEM), Fourier-transform infrared spectroscopy (FT-IR) spectroscopy, high resolution transmission electron microscopy (HR-TEM), inductively coupled plasma (ICP), thermo gravimetric analysis (TGA), vibrating sample magnetometer (VSM), and X-ray photoelectron spectroscopy (XPS). Core-shell Fe<sub>3</sub>O<sub>4</sub>@PMDP/Pd (O) nanoparticles showed excellent catalytic performance as a reusable nanocatalyst for cyanation of aryl iodides and bromides with K<sub>4</sub>[Fe(CN)<sub>6</sub>] as the cyanating agent. The nitriles were obtained in good to excellent yield and the catalyst can be recycled and reapplied up to seven times with only very slight decrease in its catalytic performance.

© 2018 Elsevier Inc. All rights reserved.

### 1. Introduction

Palladium-catalyzed coupling reactions of aryl halides have attracted widespread interest for the synthesis of organic building blocks and pharmaceutical and agrochemical derivatives. In addition to small-scale applications, there is increasing awareness of the possible application of this type of reaction for industrial fine chemical synthesis [1]. Palladium based catalysts particularly nanoscale palladium particles have recently drawn enormous attention due to their versatile role in organic synthesis [2]. The use of palladium nanoparticles in catalysis is not only industrially important [3,4], but also scientifically interesting as a result of the sensitive relationship between catalytic activity, nanoparticle size and shape as well as the nature of the surrounding media [5].

Aryl nitriles are important building blocks of numerous compounds including pharmaceutics, agrochemical materials, herbi-

\* Corresponding author. E-mail address: hojatveisi@yahoo.com (H. Veisi). cides, and dyes [6,7]. Furthermore, their easily transformation into a range of heterocycles and conversion into compounds with other functional groups such as amides, amines, aldehydes, and carboxylic acids, made them valuable and versatile intermediates in synthetic organic chemistry [8]. The most reliable and efficient approach for synthesizing aryl nitriles is transition metal catalyzed cyanation of aryl halides by cyanating agents [9]. Pd, Cu, Ni, Rh and Ir complexes are the most common transition metal catalysts used for the cyanation of aryl iodides [10–19]. Particularly; tolerance of wide functional groups in Pd catalysts, they are the most predominantly used metal catalysts for the cyanation reaction [20]. The first report on the aryl halides cyanation was documented by Takagi et al. (1973) using Pd catalyst [21]. They applied KCN as a cyanating agent at 140–150 °C [21]. Later, several sources of other cyanide ions such as CuCN, CuSCN, KCN, NaCN, and Zn(CN)<sub>2</sub> have been used for the cyanation in the presence of different Pd catalyst [22]. However, many of the cyanide sources are highly toxic. Therefore, their industrial application in the reactions is often limited. Cyanation of aryl halides by a safe cyanide source has attracted



more interest for the aryl nitriles synthesis. Recently, Beller et al. reported Pd-catalyzed cyanation of aryl halides by the use of  $K_4$ Fe(CN)<sub>6</sub>, as a non-toxic and cheaper cyanide source [23]. All the cyanide groups attached to the iron center can be coupled with aryl halides [24]. Due to its significant advantages,  $K_4$ [Fe(CN)<sub>6</sub>] has been paid increasing attention as a cyanating agent in cyanation of aryl halides [15,25–30]. Among various catalysts for the transition metal-catalyzed cyanation of aryl halides, palladium compounds have been widely investigated.

Surface functionalized magnetic iron oxide nanoparticles (NPs) are a recently emerged class of functional substances. They have been extensively applied in biotechnology and catalysis areas. Among diverse types of magnetic NPs (MNPs) adopted as the core magnetic support, specific properties of Fe<sub>3</sub>O<sub>4</sub> NPs such as high surface area, low toxicity, and superparamagnetic behavior have gained more interest [31–36]. In addition, all ferrites are metal oxides possess hydroxyl groups on their external surfaces [37]. As an outcome, well-defined shells of various substances can surround cores of ferrite. Surrounding substances can be appropriate functional groups support different types of actuators, ligands, and/or catalysts through a covalent bonding for preparing functional materials [38]. For this purpose, the magnetic-supported catalysts can show noticeable chemical stability, excellent catalytic properties, and resistance against organic solvents [39-41]. Moreover, applying an external magnetic field can retrieve them which resulted in several times reusing without any significant alteration in their catalytic activity [42].

The nm-sized metal oxides are not a selective or a suitable target for complex matrices' samples [43]. Therefore, overcoming such limitations needs a suitable coating. Furthermore, surface modification stabilizes the NPs and prevents their oxidation. However, formation of relatively stable linker between hydroxyl groups and suitable anchoring agents can efficiently functionalize MNPs. These hydroxyl groups are on the NPs surface. The anchoring agents include phosphonic acid or dopamine derivatives [44a]. Therefore, application of a lot of phenolic hydroxyl and amine functional groups are available in poly-methyldopa (PMDP) as a humic-like substance can modify MNP. In addition, in simple aqueous solutions, the feasibility of polyphenols' or catechol complexation with polyvalent cations can improve the surface properties and capacity of the Fe<sub>3</sub>O<sub>4</sub>@PMDP NPs for adsorbing and reduction of metal ions [44b]. Therefore, Fe<sub>3</sub>O<sub>4</sub>@PMDP as a nano-adsorbent has potential ability of stabilizing agent to coordinate Pd ions for making a novel magnetically separable and reusable nano-catalyst (Scheme 1). So, in the context of developing the effective and eco-friendly heterogeneous catalysts [45], we conducted synthesis of palladium nanoparticles immobilized on poly-methyldopa coated-Fe3O4 NPs (Fe3O4@PMDP/Pd (0)) as a novel core-shell nanocatalyst for cyanation of aryl halides with K4[Fe(CN)6] as the cyanating agent (Scheme 1).

### 2. Experimental section

### 2.1. Materials and apparatus

All the reagents were purchased from Aldrich and Merck and were used without any purification. The methyldopa, ferricchloridehexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O), ferrouschloridetetrahydrate (FeCl<sub>2</sub>·4H<sub>2</sub>O), sodium hydroxide, deionized water, NaCl, PdCl<sub>2</sub>,  $Na_2CO_3$ ,  $K_4[Fe(CN)_6]m$  ethanol, arylhalides were obtained from Sigma Aldrich and Merck. All reagents were of analytical grade and used without further purification. The crystalline structures of the samples were evaluated by X-ray diffraction (XRD) analysis on a Bruker D8 Advance diffractometer with CuKα radiation at 40 kV and 20 mA. Fourier transform infrared (FT-IR) spectra were recorded with a Perkin Elmer 65 spectrometer in the range of 400–4000 cm<sup>-1</sup>. Transmission electron microscopy (TEM) analysis was performed on a Phillips CM10 microscope at an accelerating voltage of 200 kV. Magnetization measurements were carried out on a BHV-55 vibrating sample magnetometer (VSM). Thermal stability of the catalyst was investigated by Thermogravimetric



Scheme 1. Preparation of Fe<sub>3</sub>O<sub>4</sub>@PMDP/Pd and its application for cyanation of aryl halides with K<sub>4</sub>[Fe(CN)<sub>6</sub>].

analysis (TGA, TSTA Type 503) at a heating rate of 10 °C/min under nitrogen atmosphere. The spectra were obtained using the Thermofisher Scientific K-Alpha XPS spectrometer. Survey spectra were initially obtained at low energy resolution (pass energy – 200 eV) followed by the main regions of interest at higher resolution (pass energy – 25 eV). A monochromatic Al K $\alpha$  X-ray was used, with a nominal spot size of 400  $\mu$ m.

# 2.2. Preparation of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>@PDA and Fe<sub>3</sub>O<sub>4</sub>@PMDP/Pd magnetic nanoparticles

The magnetic Fe<sub>3</sub>O<sub>4</sub> NPs were synthesized through the chemical coprecipitation approach [45a], and the detailed process is explained in the following. FeCl<sub>2</sub>·4H<sub>2</sub>O (2 g) and FeCl<sub>3</sub>·6H<sub>2</sub>O (5.2 g) were mixed into 25 mL deoxygenated water and 0.85 mL of concentrated HCl was added to it. The obtained solution was gradually poured into 250 mL of 1.5 M NaOH solution under agitating and N<sub>2</sub> protection at 353 K. The resulted MNPs were isolated from the mixture using a strong magnet and washed by 200 mL distilled water three times. Lastly, the products were dried at 40 °C to give Fe<sub>3</sub>O<sub>4</sub> NPs.

Fe<sub>3</sub>O<sub>4</sub> NPs (500 mg) were poured into 60 mL distilled waterethanol (2:1), following by addition of methyldopa (500 mg), and the resulted solution was agitated mechanically for 24 h at reflux condition. at the end of the reaction, the Fe<sub>3</sub>O<sub>4</sub>@PMDP NPs were separated using a magnet and rinsed with distilled water and ethanol and dried at 40 °C to give Fe<sub>3</sub>O<sub>4</sub>@PMDP.

In the next phase, 500 mg of prepared Fe<sub>3</sub>O<sub>4</sub>@PMDP was sonically dispersed in distilled water (100 mL) for 20 min. Consequently, 0.02 g Na<sub>2</sub>PdCl<sub>4</sub> was dissolved in 20 mL water and added to reaction solution and agitated for 24 h at reflux conditions. In the next step, Fe<sub>3</sub>O<sub>4</sub>@PMDP/Pd(0) was magnetically isolated and rinsed with ethanol, deionized water and acetone, respectively to remove probable unattached substrates. Furthermore, the palladium level of the catalyst was determined 0.28 ± 0.001 mmol g<sup>-1</sup> by means of atomic absorption spectroscopy.

### 2.3. General procedure for cyanation reactions

A solution containing  $K_4[Fe(CN)_6]$  (0.17 mmol), aryl halide (1.0 mmol),  $Na_2CO_3$  (1.5 mmol),  $Fe_3O_4@PMDP/Pd$  (45 mg, 1.5 mol%), and DMF (3 mL) was mixed under stirring at 120 °C for the specified time. TLC was used to follow the reaction. At the end of the reaction, the obtained solution was cooled to ambient temperature and filtered, and the residue was rinsed using ethyl acetate ( $3 \times 10$  mL) to isolate the catalyst using a suitable magnet. Water phase containing ethyl acetate (30 mL) was mixed with the organic phase to extreact the ethyl acetate from the water. The organic phase was dried over  $Na_2SO_4$ . The products were resulted by evaporating the organic solvent. If more purification was needed, the products were passed through a short silica gel column using the eluent of *n*-hexane. All the products are known substances and were compared with authentic specimens.

### 3. Results and discussion

This research has been aimed to continue our earlier research [45] and design a new magnetic nanocomposite using the influence of both coordinator and stabilizer agent for immobilizing metal ions, e.g. palladium. Firstly,  $Fe_3O_4$  NPs was synthesized according to our earlier report [45a]. Next,  $Fe_3O_4$  NPs were immobilized using PMDP, in *situ*, through polymerization of methyldopa in water/ethanol (2:1) under reflux condition. Then, the synthesized  $Fe_3O_4$ @PMDP nanocomposite was used for absorbing palladium ions on their PMDP layers. The palladium

ions were instantly reduced to metallic Pd NPs using the advantage of the existing active catechol and amine groups, *in situ*. In the final phase, the Fe<sub>3</sub>O<sub>4</sub>@PMDP/Pd nanocatalyst were isolated using a suitable magnet and dried under vacuum. The synthetic route of the catalyst is summarized in Scheme 1. The palladium content of the nanocomposite was  $0.28 \pm 0.001$  mmol g<sup>-1</sup> as obtained with atomic absorption spectroscopy. The FTIR, X-ray photoelectron spectroscopy (XPS), FESEM, EDX, HR-TEM, TGA, ICP and VSM were used to characterize the catalyst.

FT-IR is used for studying the surface composition of the prepared Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>@PMDP; and Fe<sub>3</sub>O<sub>4</sub>@PMDP/Pd(II) NPs. In the spectrum of naked Fe<sub>3</sub>O<sub>4</sub> (Fig. 1), the strong peak observed at 582 and 632  $\text{cm}^{-1}$  are corresponded to the vibration of the Fe–O groups and the peaks appeared at 1625 and 3385 cm<sup>-1</sup> are related with the surface-adsorbed water and hydroxyl groups [45a]. The FTIR spectra of Fe<sub>2</sub>O<sub>4</sub>@PMDP and Fe<sub>2</sub>O<sub>4</sub>@PMDP/Pd (Fig. 1b and c) display Fe-O vibrations in the similar vicinity. The peaks appeared at 3380, 2928, 1600, 1465  $\text{cm}^{-1}$  can be allocated to O-H stretching, C-H stretching, C=C stretching and C-N stretching relating to the existence of functional groups -OH of phenol and -C=C-NH- in the Fe<sub>3</sub>O<sub>4</sub>@PMDP [45a]. As can be observed, the broad peak appeared at  $\sim$ 2400–3400 cm<sup>-1</sup> are because of asymmetric and symmetric stretching of the COOH and N-H stretching, which show the existence of bound amino acid on the MNP surface (Fig. 1b and c). However, the peaks observed at 1600 and 1512 cm<sup>-1</sup> can be allocated to the vibration of benzene ring skeleton [45a]. These outcomes offer that immobilization of PMDP polymer on the surface of Fe<sub>3</sub>O<sub>4</sub> NPs was performed effectively. Furthermore, the band at about 1656 cm<sup>-1</sup>, which relates to COOH bond of the supported PMDP (Fig. 1b), is moved to lower wavenumbers  $(1638 \text{ cm}^{-1})$  (Fig. 1c), signifying a good interaction between carboxylic group and Pd NPs. Moreover, the bending vibration absorption band corresponding to N-H at 1436 cm<sup>-1</sup> (Fig. 1b) was moved to lower wavenumbers (1436  $\rightarrow$  1430), which is probably because of the interaction of an amine group with Pd NPs (Fig. 1c). Considering the above results, it can be stated that the Fe<sub>2</sub>O<sub>4</sub>@PMDP/Pd nanocomposite was effectively synthesized along with a strong interaction between amino acid, catechol and amino groups of the supported PMDP and the Pd NPs. This



Fig. 1. FT-IR spectra of (a) Fe<sub>3</sub>O<sub>4</sub>, (b) Fe<sub>3</sub>O<sub>4</sub>@PMDP, and (c) Fe<sub>3</sub>O<sub>4</sub>@PMDP/Pd.



Fig. 2. (a) SEM and (b) TEM image of Fe<sub>3</sub>O<sub>4</sub>@PMDP/Pd.



Fig. 3. EDX data for  $Fe_3O_4@PMDP/Pd$ .

observation was confirmed by the results of TEM, SEM and XPS analysis.

The scanning electron microscopy (SEM) was applied for studying size and morphology of Fe<sub>3</sub>O<sub>4</sub>@PMDP/Pd. The SEM image of Fe<sub>3</sub>O<sub>4</sub>@PMDP/Pd presented that the synthesized catalyst is nanometer quasi-spherical with a mean diameter of  $\sim$ 90 ± 5 nm (Fig. 2a). Furthermore, a continuous polymer layer can be observed on the surface. Moreover, TEM images corresponding to Fe<sub>3</sub>O<sub>4</sub>@-PMDP/Pd is showed in Fig. 2b. This Figure shows that a PMDP coating of about 3 nm-in-thickness has apparently immobilized the surface of Fe<sub>3</sub>O<sub>4</sub> NPs. Consequently, Fe<sub>3</sub>O<sub>4</sub>@PMDP NPs have produced a core/shell structure. Furthermore, the Pd NPs were in situ reduced and its immobilization on Fe<sub>3</sub>O<sub>4</sub>@PMDP surface was performed via agitating a solution containing Fe<sub>3</sub>O<sub>4</sub>@PMDP and Na<sub>2</sub>-PdCl<sub>4</sub>, at 100 °C for 24 h. During this procedure, the PMDP shell layer had served to reduce palladium ions and cap the particles. TEM, EDX, and XPS proved that Pd NPs have been immobilized on Fe<sub>3</sub>O<sub>4</sub>@PMDP surface, visually.



Fig. 4. Elemental mapping of Fe<sub>3</sub>O<sub>4</sub>@PMDP/Pd shows the presence of Fe, O, C, N and Pd atoms in the nanocomposite.

In addition, the EDX detector combined with the SEM was applied for proving the existence of PMDP shell and palladium species on the  $Fe_3O_4$  NPs surface that the outcomes proved the presence of Fe, C, and O in Fig. 3. The presence of the Pd signals in the nanocatalyst's EDX (Fig. 3) presented the effective synthesis of desired  $Fe_3O_4@PMDP/Pd$  catalyst.

Additionally, SEM along with wavelength-dispersive X-ray spectroscopy (WDX) was used for obtaining several qualitative information on distribution of numerous elements of the catalyst matrix. Fig. 4 shows the representative SEM images and elemental WDX maps corresponding to the prepared nanocatalyst. The WDX maps indicate that Pd NPs (according to XPS outcome) are completely dispersed in the composite matrix. Also, selected-area elemental analysis approves homogenous presence of C, N, O and Fe throughout the nanocomposites, and therefore, the samples are prepared regular and uniformity.

XPS is a powerful instrument for investigation of the electronic features of the species formed on the surface, such as the electron environment, oxidation state, and the binding energy of the core electron of the metal. Fig. 5 shows the XPS elemental survey scans of the surface of the Fe<sub>3</sub>O<sub>4</sub>@PMDP/Pd catalyst. The peaks corresponded to oxygen, carbon, nitrogen, palladium and iron are clearly seen in this spectrum. Moreover, XPS analysis was carried out for determining the oxidation state of the Pd. In Fig. 5, the Pd binding energy of Fe<sub>3</sub>O<sub>4</sub>@PMDP/Pd indicates two peaks centered at 335.24 and 341.67 eV relating to Pd  $3d_{3/2}$  and Pd  $3d_{5/2}$ , respectively. According to the earlier research [46,47], these peaks related to Pd(0) species, which have capped by polymer groups. In other words, all Pd atoms are shown in their reduced forms, which confirms effective reduction of Pd(II) to Pd(0) NPs by PMDP layers (Fig. 5, inset). Presence of PMDP in the structure of Fe<sub>3</sub>O<sub>4</sub>@PMDP/ Pd is re-confirmed by XPS analysis due to observation of C<sub>1</sub>s, N 1s in the spectrum.

In order to establish the reaction between catechol groups and palladium ions, we studied the high-resolution XPS spectra of C 1s in Fe<sub>3</sub>O<sub>4</sub>@PMDP and Fe<sub>3</sub>O<sub>4</sub>@PMDP/Pd respectively (Fig. 6a and b). For C 1s in Fe<sub>3</sub>O<sub>4</sub>@PMDP, the ratio of phenolic quinone (C=O) to hydroxyl groups(C-OH) was around 1.12, but the ratio was up to 1.45 for that in Fe<sub>3</sub>O<sub>4</sub>@PMDP/Pd. The outcome clarified that the value of phenolic quinone enhanced along with the reduction of the value of phenolic hydroxyl following reduction reaction. This data obviously confirmed the incidence of galvanic replacement reaction between catechol groups and palladium ions.



Fig. 6. XPS spectra of  $Fe_3O_4@PMDP$  and  $Fe_3O_4@PMDP/Pd$ : survey spectrum of (a) C 1s in  $Fe_3O_4@PMDP$ ; and (b) C 1s in  $Fe_3O_4@PMDP/Pd$ .

It was seen that both synthesized particles have slight coercivities, which indicate their superparamagnetic nature. As can be found in Fig. 7, saturation magnetizations of  $Fe_3O_4$  and  $Fe_3O_4@$ -PMDP/Pd are 61.9 and 54.6 emu g<sup>-1</sup>, respectively. The order is due to a rise in the level of non-magnetic materials on the particle surface that causes higher percentage of the non-magnetic PMDP coating and the grafted catalyst layer.

The stability of the synthesized Fe<sub>3</sub>O<sub>4</sub>@PMDP/Pd nanocatalyst and also percent of organic functional groups on the magnetic NPs surface were studied using TGA analysis. The catalyst TGA curve (Fig. 8) shows a primary weight loss of 6.5% up to 185 °C which is because of physically adsorbed solvent and surface hydroxyl groups on the support. Thermal degradation of the catalyst happened following 200 °C which shows the high thermo-



Fig. 5. XPS spectrum related to the elemental survey scan of Fe<sub>3</sub>O<sub>4</sub>@PMDP/Pd and in the Pd 3d region (inset).

stability of catalyst. The second and third weight loss of 42% over the range of 200–600  $^{\circ}$ C was due to degrading the organic remains.

After structural characterization of the prepared metal-polymer composite ( $Fe_3O_4@PMDP/Pd$ ), and because of our ongoing interest on the biosynthesis of metal NPs and heterogeneous catalysts [45],



Fig. 7. VSM spectra of (a) Fe<sub>3</sub>O<sub>4</sub> and (b) Fe<sub>3</sub>O<sub>4</sub>@PMDP/Pd.



#### Table 1

The optimization of reaction parameters for cyanation of 4-iodotoluene using  $K_4[Fe(CN)_6]$  catalyzed by  $Fe_3O_4@PMDP/Pd^a.$ 



Entry	Pd (mol%)	Solvent	Base	T (°C)	Time (h)	Yield (%) <sup>b</sup>
1	1.5	DMF	K <sub>2</sub> CO <sub>3</sub>	120	5	85
2	1.5	Toluene	K <sub>2</sub> CO <sub>3</sub>	120	12	35
3	1.5	EtOH	K <sub>2</sub> CO <sub>3</sub>	120	12	25
4	1.5	$H_2O$	K <sub>2</sub> CO <sub>3</sub>	120	24	30
5	1.5	CH₃CN	K <sub>2</sub> CO <sub>3</sub>	120	8	80
6	1.5	Xylene	K <sub>2</sub> CO <sub>3</sub>	120	12	55
7	1.5	DMF	NaOAc	120	8	40
8	1.5	DMF	Et <sub>3</sub> N	120	12	25
9	1.5	DMF	Na <sub>2</sub> CO <sub>3</sub>	120	2	96
10	1.5	DMF	NaOH	120	24	25
11	1.5	DMF	No base	120	24	Trace
12	1.5	DMF	$Na_2CO_3$	100	8	80
13	1.5	DMF	$Na_2CO_3$	80	12	65
14	1.5	DMF	$Na_2CO_3$	25	24	25
15	1.0	DMF	Na <sub>2</sub> CO <sub>3</sub>	120	8	80
16	2.0	DMF	Na <sub>2</sub> CO <sub>3</sub>	120	2	96
17	0.0	DMF	Na <sub>2</sub> CO <sub>3</sub>	120	24	0

 $^a$  Reaction conditions: 4-lodotoluene (1.0 mmol),  $K_4[Fe(CN)_6]$  (0.17 mmol), catalyst, base (1.5 mmol) and solvent (3 mL) for 2 h.

<sup>b</sup> Isolated yield.

its catalytic performance was examined for synthesis of benzonitriles by the cyanation of aryl halides with  $K_4[Fe(CN)_6]$  as the cyanating agent (Scheme 1). To attain optimum conditions, the reaction of 4-iodotoluene and K<sub>4</sub>[Fe(CN)<sub>6</sub>] in the existence of Fe<sub>3</sub>-O4@PMDP/Pd catalyst was chosen as a model reaction and the influence of different reaction factors like solvent, base, temperature and the level of catalyst were examined in detail. The outcomes of optimization study have been given in Table 1. As observed, no case product was detectable with no use of the catalyst (Table 1, entry 17). Though, introducing the catalyst to the reaction mixture quickly developed preparation of the product in excellent yields. The reactions were performed in DMF as the optimum solvent. Amongst the investigated bases, Na<sub>2</sub>CO<sub>3</sub> was the most effective base. Additionally, the influence of catalyst loading was studied in the catalyst amounts range from 1.0 mol% to 2.0 mol% (Table 1, entries 9, 15 and 16). Based on the results, the maximum performance can be achieved using 0.045 g of the catalyst which is equal to 1.5 mol% (Table 1, entry 9). Furthermore, the optimal reaction temperature was found to be 120 °C (entry 9 versus entries 12-14). Lower yield of the desired product was studied at 25 °C reaction temperature (Table 1, entry 14). It was found that it was not necessary to use an excess of K<sub>4</sub>Fe(CN)<sub>6</sub>, as each mole of

# Table 2 $\label{eq:constraint} Fe_3O_4@PMDP/Pd \mbox{ catalyzed cyanation of aryl halides using $K_4[Fe(CN)_6]^a$.}$



Entry	Aryl halide	Yield (%) <sup>b</sup>	TOF $(h^{-1})^c$	Ref. <sup>d</sup>
1	C <sub>6</sub> H <sub>5</sub> I	96	32	[48]
2	C <sub>6</sub> H <sub>5</sub> Br	85	28.3	[48]
3	C <sub>6</sub> H <sub>5</sub> Cl	Trace	-	[48]
4	p-NCC <sub>6</sub> H <sub>4</sub> I	96	32	[50]
5	p-NCC <sub>6</sub> H <sub>4</sub> Br	90	30	[50]
6	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> I	90	30	[24]
7	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Br	85	28.3	[24]
8	p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> I	95	31.7	[24]
9	p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> Br	92	30.7	[24]
10	p-ClC <sub>6</sub> H <sub>4</sub> I	96	32	[50]
11	p-ClC <sub>6</sub> H <sub>4</sub> Br	92	30.7	[50]
12	o-CH3OC6H4I	92	30.7	[49]
13	o-CH3OC6H4Br	88	29.3	[49]
14	4-Iodopyridine	85	28.3	[51]
15	3-Iodopyridine	90	30	[51]

<sup>a</sup> Reaction conditions: Arylhalide (1.0 mmol),  $K_4$ [Fe(CN)<sub>6</sub>] (0.17 mmol),  $Na_2CO_3$  (1.5 mmol),  $Fe_3O_4@PMDP/Pd$  (1.5 mol%) were stirred in DMF (3.0 mL) at 120 °C for 2 h.

<sup>b</sup> Isolated yield.

<sup>c</sup> TOF, turnover frequencies (TOF = (Yield/Time)/Amount of catalyst (mol).

<sup>d</sup> Earlier reference of the corresponding product.



Fig. 9. The recycling of the Fe<sub>3</sub>O<sub>4</sub>@PMDP/Pd.

 $K_4$ Fe(CN)<sub>6</sub> contained six cyanide ions. Therefore, the ratio of  $K_4$ Fe (CN)<sub>6</sub> to aryl halide was 0.17:1. With the excess  $K_4$ Fe(CN)<sub>6</sub>, There was no significant change in the reaction time and reaction yield.

Having the successful optimized reaction conditions in hand, investigation of the substrate scopes for the cyanation reaction has started. Numerous benzonitriles were prepared exclusively with good turnover frequencies (TOF) using the cyanation of aryl iodides and aryl bromides. The outcomes have been listed in the Table 2. Electron-releasing (Table 2, entries 6, 8, 12), electron-withdrawing (Table 2, entries 4, 10) and sterically hindered aryl iodides (Table 2, 12, 13) were completely tolerated under the

optimal reaction conditions. The reaction of electron-poor nitrogen heterocycles, 4-iodopyridine and 3-iodopyridine proceeded in good yield (Table 2, entries 14, 15). Aryl bromides were similarly reactive, but aryl chlorides were unreactive permitting selective reactions for 1-chloro-4-iodobenzene (Table 2, entry 10) and 1-bromo-4-chlorobenzene (Table 2, entry 11). Furthermore, due to the weakness of the carbon-iodide bond in aryl iodides, these compounds show more reactivity than aryl bromides.

The catalyst recyclability is important in terms of commercial applications. At this point, the catalyst recyclability and recovery have been examined through reaction of 4-iodotoluene and



Fig. 10. TEM and EDX analysis of reused catalyst after the 7th run.



Scheme 2. Proposed mechanism based on Beller's works for Fe<sub>3</sub>O<sub>4</sub>@PMDP/Pd catalyzed cyanation of aryl halides.

 $K_4[Fe(CN)_6]$  as a model reaction. As can be expected, the catalyst showed a good recyclability with no considerable change in its activity (Fig. 9) and by an external magnet the catalyst was separated from the reaction mixture, washed with ethanol and warmish water, and reapplied in a desired reaction. The ICP analysis showed that the palladium level of the catalyst following catalysis has not changed considerably (the level of palladium was 2.91 wt% (0.27 mmol/g), presenting that no significant palladium leaching to the solution occurs over the catalytic processions. Therefore, in overall, it can be said that polymethyldopa layers stabilized Pd NPs against aggregation and leaching, thus maintaining the catalytic activity.

Furthermore, to characterize the catalyst heterogeneity, for the cyanation reactions, a hot filtration test was performed using Fe<sub>3</sub>- $O_4@PMDP/Pd$  between 4-iodotoluene and  $K_4[Fe(CN)_6]$  under the optimal conditions. A reaction vield of 65% could be achieved after 60 min, and then the catalyst was isolated to be reused. No enhance in performance of the product was found and when the reaction was continued for another 60 min after separation of the catalyst, the heterogeneous property of the catalyst was approved. The TEM and EDX analysis (Fig. 10) of the catalyst after the seven cycles showed the preservation of the catalyst's nanostructure.

A probable mechanism based on Beller's works [10,24], for the Fe<sub>3</sub>O<sub>4</sub>@PMDP/Pd-catalyzed cyanation reaction includes a famous mechanism corresponding to cyanation of aryl halides which happens on the catalyst surface (Scheme 2). Reaction proceeded via the oxidative addition of aryl halide over catalyst followed by cyanide anion transfer from  $K_4[Fe(CN)]_6$  and finally reductive elimination step afforded the aryl cyanide product.

### 4. Conclusion

In conclusion, the new magnetic interphase nanocatalyst of palladium nanoparticles immobilized on magnetic Fe<sub>3</sub>O<sub>4</sub> NPs modified by PMDP Fe<sub>3</sub>O<sub>4</sub>@PMDP/Pd was effectively prepared and characterized using diverse analytical methods. It was indicated that Fe<sub>3</sub>O<sub>4</sub>@PMDP/Pd can be used as a green, useful and recoverable heterogeneous magnetic nanocatalyst for cyanation of aryl iodides and aryl bromides using K<sub>4</sub>[Fe(CN)<sub>6</sub>] as the cyanating agent. The nitriles were yielded good to excellent and the catalyst can be recycled and reused several times.

#### Acknowledgments

We are thankful to Payame Noor University for partial support of this work.

#### References

- [1] (a) J.G. de Vries, Can. J. Chem. 79 (2001) 1086–1092;
   (b) M. Beller, A. Zapf, W. Magerlein, Chem. Eng. Technol. 24 (2001) 575–582; (c) A. Zapf, M. Beller, Top. Catal. 19 (2002) 101–109.
- [2] (a) J. Tsuji, Palladium Reagents and Catalysts, John Wiley & Sons Ltd, Chichester, UK, 2004;
  - (b) D. Astruc, F. Lu, J.R. Aranzaes, Angew. Chem. Int. Ed. Engl. 44 (2005) 7852; (c) H. Veisi, J. Gholami, H. Ueda, P. Mohammadi, M. Noroozi, J. Mol. Catal. A: Chem. 396 (2015) 216:
  - (d) H. Veisi, M. Hamelian, S. Hemmati, J. Mol. Catal. A: Chem. 395 (2014) 25; (e) D. Wang, D. Astruc, Chem. Rev. 114 (2014) 6949;
  - (f) H. Veisi, N. Morakabati, New J. Chem. 39 (2015) 2901.
- [3] H. Liu, X. Chen, L. Huang, J. Wang, H. Pan, Electroanalysis 26 (2014) 556-564.
- [4] Y. Liu, J. Huang, D. Wang, H. Hou, T. You, Anal. Methods 2 (2010) 855–859. [5] K. Reddaiah, T.M.K. Mallikarjuna, G. Narasimha, Anal. Methods 5 (2013) 5627-5636.
- [6] A. Kleemann, J. Engel, B. Kutscher, D. Reichert, Pharmaceutical Subtances: Syntheses, Patents, Applications, fourth ed., Georg Thieme, Stuttgart, 2001.
- [7] S.J. Collierm, P. Langer, Sci. Synth. 19 (2004) 403.
- [8] Z. Rappoport, Chemistry of the Cyano Group, first ed., John Wiley & Sons, London, 1970.
- [9] G. Yan, J. Yu, L. Zhang, Youji Huaxue 32 (2012) 294-303.

- [10] M. Sundermeier, A. Zapf, S. Mutyala, W. Baumann, J. Sans, S. Weiss, M. Beller, Chem. Eur. J. 9 (2003) 1828-1836.
- [11] H.-J. Cristau, A. Ouali, J.-F. Spindler, M. Taillefer, Chem. Eur. J. 11 (2005) 2483-2492
- [12] Y. Ren, Z. Liu, S. Zhao, X. Tian, J. Wang, W. Yin, S. He, Catal. Commun. 10 (2009) 768-771
- [13] T. Schareina, A. Zapf, W. Mägerlein, N. Müller, M. Beller, Chem. Eur. J. 13 (2007) 6249-6254.
- [14] J. Zanon, A. Klapars, S.L. Buchwald, J. Am. Chem. Soc. 125 (2003) 2890-2891.
- [15] Q. Wen, J. Jin, Y. Mei, P. Lu, Y. Wang, Eur. J. Org. Chem. (2013) 4032–4036.
- [16] M. Gholinejad, A. Aminianfar, J. Mol. Catal. A Chem. 397 (2015) 106-113.
- [17] Z. Jiang, Q. Huang, S. Chen, L. Long, X. Zhou, Adv. Synth. Catal. 354 (2012) 589-592.
- [18] A.B. Pawar, S. Chang, Chem. Commun. 50 (2014) 448-450.
- [19] R.K. Arvela, N.E. Leadbeater, J. Org. Chem. 68 (2003) 9122-9125.
- [20] (a) A. Sekiya, N. Ishikawa, Chem. Lett. 3 (1975) 277-278; (b) J.R. Dalton, S.L. Regen, J. Org. Chem. 44 (1979) 4443-4444; (c) N. Chatani, T. Hanafusa, J. Org. Chem. 51 (1986) 4714-4716; (d) V. Nair, D.F. Purdy, T.B. Sells, J. Chem. Soc., Chem. Commun. (1989) 878879: (e) D.M. Tschaen, R. Desmond, A.O. King, M.C. Fortin, B. Pipik, S. King, T.R. Verhoeven, Synth. Commun. 24 (1994) 887890; (f) G.-Y. Zhang, J.-T. Yu, M.-L. Hu, J. Cheng, J. Org. Chem. 78 (2013) 2710-2714; (g) Z. Zhang, L.S. Liebeskind, Org. Lett. 8 (2006) 4331-4333; (h) M. Sundermeier, A. Zapf, M. Beller, Angew. Chem., Int. Ed. 42 (2003) 1661-1664: (i) S. Zheng, C. Yu, Z. Shen, Org. Lett. 14 (2012) 3644-3647.
- [21] K. Takagi, T. Okamoto, Y. Sakakibara, S. Oka, Chem. Lett. 5 (1973) 471-474. [22] (a) P. Anbarasan, T. Schareina, M. Beller, Chem. Soc. Rev. 40 (2011) 5049-5067:
- (b) M. Sundermeier, A. Zapf, M. Beller, Eur. J. Inorg. Chem. 19 (2003) 3513-3526.
- [23] T. Schareina, A. Zapf, M. Beller, Chem. Commun. 12 (2004) 1388-1389.
- [24] T. Schareina, A. Zapf, M. Beller, J. Organomet. Chem. 689 (2004) 4576–4583.
- [25] G. Yan, C. Kuang, Y. Zhang, J. Wang, Org. Lett. 12 (2010) 1052.
- [26] P.-Y. Yeung, C.-M. So, C.-P. Lau, F.-Y. Kwong, Angew. Chem. Int. Ed. 49 (2010) 8918.
- [27] K. Chattopadhyay, R. Dey, B.C. Ranu, Tetrahedron Lett. 50 (2009) 3164.
  - [28] C. Deblase, N.E. Leadbeater, Tetrahedron 66 (2010) 1098.
  - [29] J. Wang, J. Ma, X. Tian, W. Yin, Adv. Synth. Catal. 354 (2012) 2301.
  - [30] X. Tian, Y. Sun, C. Dong, K. Zhang, T. Liang, Y. Zhang, C. Hou, Chem. Lett. 41 (2012) 719.
  - [31] (a) M. Bagherzadeh, A. Mortazavi-Manesh, RSC Adv. 6 (2016) 41551; (b) C.O. Dalaigh, S.A. Corr, Y. Gunko, S.J. Connon, Angew. Chem. Int. Ed. 46 (2007) 4329-4332
  - [32] S. Luo, X. Zheng, H. Xu, X. Mi, L. Zhang, J.-P. Cheng, Adv. Synth. Catal. 349 (2007) 2431-2434.
  - [33] S. Shylesh, V. Schunemann, W.R. Thiel, Angew. Chem. Int. Ed. 49 (2010) 3428-3452.
  - [34] B. Abbas Khakiani, K. Pourshamsian, H. Veisi, Appl. Organometal. Chem. 29 (2015) 259.
  - [35] Y. Zhu, L.P. Stubbs, F. Ho, R. Liu, C.P. Ship, J.A. Maguire, N.S. Hosmane, Chem. Cat. Chem. 2 (2010) 365–374.
  - [36] C.W. Lim, I.S. Lee, Nano Today 5 (2010) 412-434.
  - [37] E. McCafferty, J.P. Wightman, Surf. Interface Anal. 26 (1998) 549-564.
  - [38] P. Riente, C. Mendozaa, M.A. Peric, J. Mater. Chem. 21 (2011) 7350-7355.
  - [39] (a) K.K. Senapati, S. Roy, C. Borgohain, P. Phukan, J. Mol. Catal. A Chem. 352 (2012) 128–134;
  - (b) E. Farzad, H. Veisi, J. Indus. Eng. Chem. 60 (2018) 114-124.
  - [40] (a) D. Lee, J. Lee, H. Lee, S. Jin, T. Hyeon, B.M. Kim, Adv. Synth. Catal. 348 (2006) 41-46:
    - (b) R.K. Sharma, S. Dutta, S. Sharma, R. Zboril, R.S. Varma, M.B. Gawande, Green Chem. 18 (2016) 3184: (c) V. Polshettiwar, R. Luque, A. Fihri, H. Zhu, M. Bouhrara, J.-M. Basset, Chem.
    - Rev. 111 (2011) 3036:
    - (d) D. Wang, D. Astruc, Chem. Rev. 114 (2014) 6949.
  - [41] R. Abu-Rezig, H. Alper, D. Wang, M.L. Post, J. Am. Chem. Soc. 128 (2006) 5279-5282.
  - [42] E. Karaoğlu, A. Baykal, H. Erdemi, L. Alpsoy, H. Sözeri, J. Alloys Compd. 509 (2011) 9218 - 9225.
  - [43] K. Aguilar-Arteaga, J.A. Rodriguez, E. Barrado, Anal. Chim. Acta 674 (2010) 157
  - [44] (a) S. Mazurm, A. Barras, V. Kuncser, A. Galatanu, V. Zaitzev, K.V. Turcheniuk, P. Woisel, J. Lyskawa, W. Laure, A. Siriwardena, R. Boukherroub, S. Szunerits, Nanoscale 5 (2013) 2692; (b) M. Bagtash, Y. Yamini, E. Tahmasebi, J. Zolgharnein, Z. Dalirnasab, Microchim, Acta 183 (2016) 449.
  - [45] (a) H. Veisi, S. Taheri, S. Hemmati, Green Chem, 18 (2016) 6337:
    - (b) F. Bonyasi, M. Hekmati, H. Veisi, J. Colloid. Interface Sci. 496 (2017) 177;
      - (c) E. Farzad, H. Veisi, J. Indus. Eng. Chem. 60 (2018) 114-124;
      - (d) M. Shahriary, H. Veisi, M. Hekmati, S. Hemmati, Mat. Sci. Eng. C. 90 (2018) 57-66:
    - (e) H. Veisi, A. Sedrpoushan, S. Hemmati, Appl. Organomet. Chem. 29 (2015) 825;
    - (f) M. Pirhayati, H. Veisi, A. Kakanejadifard, RSC Adv. 6 (2016) 27252;
    - (g) H. Veisi, S. Azizi, P. Mohamadi, J. Clean. Prod. 170 (2018) 1536-1543;

(h) F. Heidari, M. Hekmati, H. Veisi, J. Colloid Interface Sci. 501 (2017) 175–184;

(i) H. Veisi, S.A. Mirshokraie, H. Ahmadian, Int. J. Biol. Macromol. 108 (2018) 419-425;

(i) S. Lebaschi, M. Hekmati, H. Veisi, J. Colloid, Interface Sci. 485 (2017) 223;
(k) H. Veisi, M. Pirhayati, A. Kakanejadifard, P. Mohammadi, M.R. Abdi, J. Gholami, S. Hemmati, ChemSelect 3 (2018) 1820–1826;

(1) H. Veisi, A. Rashtiani, V. Barjasteh, Appl. Organometal. Chem. 30 (2016) 231;

(m) H. Veisi, D. Kordestani, S. Sajjadifar, M. Hamelian, Iran. Chem. Commun. 2 (2014) 27.

- [46] J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, Handbook of X-ray Photoelectron Spectroscopy, Physical Electronics Inc, USA, 1995, pp. 118–119.
- [47] H. Veisi, S. Najafi, S. Hemmati, Int. J. Biol. Macromol. 113 (2018) 186-194.
- [48] K. Niknam, A. Deris, F. Panahi, Chinese J. Catal. 34 (2013) 718–722.
  [49] D. Ganapathy, S. Srinivas Kotha, G. Sekar, Tetrahedron Lett. 56 (2015) 175–178.
- [50] M. Nasrollahzadeh, S.M. Sajadi, J. Colloid Interface Sci. 469 (2016) 191–195.
  [51] M. Nasrollahzadeh, Tetrahedron Lett. 57 (2016) 337–339.