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In *situ* immobilized palladium nanoparticles on surface of poly-methyldopa coated-magnetic nanoparticles (Fe_3O_4@PMDA/Pd): A magnetically recyclable nanocatalyst for cyanation of aryl halides with $K_4[Fe(CN)_6]$

Hojat Veisi *, Saba Hemmati, Parisa Safarimehr

Department of Chemistry, Payame Noor University, Tehran, Iran

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ABSTRACT

Poly-methyldopa (PMDP)-coated Fe_3O_4 nanoparticles (Fe_3O_4@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_3O_4@PMDP as a core-shell magnetic coordinator and stabilizer agent. In this protocol, Pd ions were adsorbed on surfaces of Fe_3O_4@PMDP through immersion of the PMDP-coated Fe_3O_4 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_3O_4@PMDP/Pd (0) nanoparticles showed excellent catalytic performance as a reusable nanocatalyst for cyanation of aryl iodides and bromides with $K_4[Fe(CN)_6]$ 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.

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, herbicides, 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 $Zn(CN)_2$ 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

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* Corresponding author.
E-mail address: hojatveisi@yahoo.com (H. Veisi).

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more interest for the aryl nitriles synthesis. Recently, Beller et al. reported Pd-catalyzed cyanation of aryl halides by the use of $K_4Fe(CN)_6$, 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, $K_4[Fe(CN)_6]$ 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.

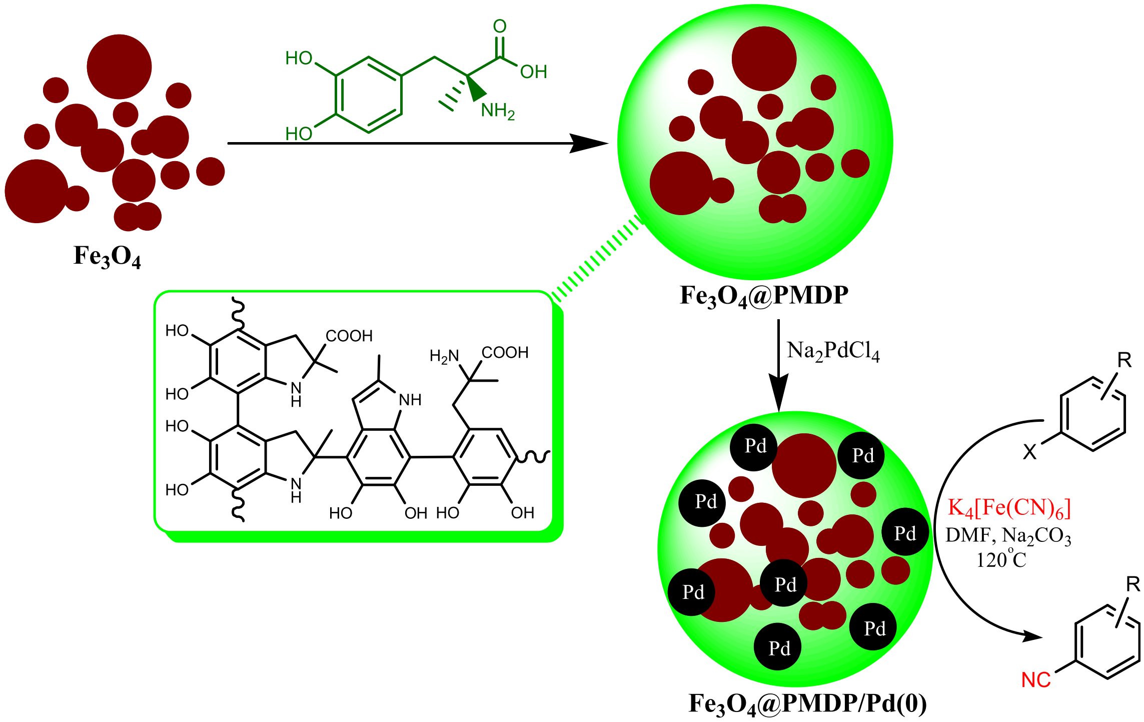
Surface functionalized magnetic iron oxide nanoparticles (NPs) are a recently emerged class of functional substances. They have been extensively applied in biotechnology and catalysis areas. Among diverse types of magnetic NPs (MNPs) adopted as the core magnetic support, specific properties of Fe_3O_4 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_3O_4@PMDP NPs for adsorbing and reduction of metal ions [44b]. Therefore, Fe_3O_4@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 ($FeCl_3{\cdot}6H_2O$), ferrouschloridetetrahydrate ($FeCl_2{\cdot}4H_2O$), sodium hydroxide, deionized water, NaCl, $PdCl_2$, 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^{-1}. 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_3O_4@PMDP/Pd and its application for cyanation of aryl halides with $K_4[Fe(CN)_6]$.