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Preparation and characterization of Fe_3O_4@SiO_2@PMA:AS an efficient and recyclable nanocatalyst for the synthesis of 1-amidoalkyl-2-naphthols

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ABSTRACT

In this paper, we report a method for preparation of functionalized superparamagnetic Fe_3O_4@SiO_2 that is synthesized based on several stages. First of all, the Fe_3O_4@SiO_2 nanosphere core-shell is synthesized. Then, $H_3PMo_{12}O_{40}$ nanoparticles were synthesized by the treatment of $H_3PMo_{12}O_{40}$ with *n*-Octane as solvent by a solvothermal method and this nano hetero polyacid immobilized onto the imidazole functionalized Fe_3O_4@SiO_2 nanoparticles. The structure of the samples was characterized by XRD, TEM, DLS, FE-SEM, FT-IR, N_2 adsorption–desorption isotherm analysis and VSM. Moreover, an efficient and direct protocol is described for the preparation of amidoalkyl naphthols employing a multi-component, one-pot condensation reaction of β-naphthol, aldehydes and acetamide, benzamide and urea in the presence of Fe_3O_4@SiO_2-imid-PMA^n under solvent-free and microwave conditions. Also, nanocatalyst can be easily recovered by a magnetic field and reused for the next reactions for at least 5 times without distinct deterioration in catalytic activity.

1. Introduction

Nanomaterials have been interested extensively because of their unique properties [1] and used extensively in biology [2], physics [3] and chemistry [4]. Also, nanoparticles have gained an interest because of their potential applications in areas such as ceramics [5], optics [6], electronics [7], magnetic data storage [8], catalysis [9–11] and nanocomposites. When size of the particle is decreased to nanometer scale, the surface area of them significantly increased and those activities could be improved [12].

In the past decade, the synthesis of superparamagnetic nanoparticles had been intensively developed due to their different applications such as magnetic inks for jet printing [13], targeted drug delivery [14,15], contrast agents in magnetic resonance imaging (MRI) [16], catalysts for carbon nanotube formation[17], sorbents for environmental remediation [18,19] and hyperthermia treatment of cancer cells [20]. These applications attributed to those unique properties, such as size, superparamagnetism, the crystallinity, size distribution and monodispersity. Currently, much attention has been focused on the synthesis of magnetic metal oxide structures that coating with a silica shell [21]. In contrast to most of the solid catalysts that their recovery and reusability are very difficult, recovery and reusability of core-shell nanostructure magnetic catalysts could be easily carried out under magnetic field. Therefore, the magnetic core–shell structures are a good supports for the catalysts [22].

In recent years, brønsted acids such as Keggin-type heteropolyacids have been used as efficient catalysts for a variety of organic reactions because of their superacidic and redox properties, low toxicity, ease of handling, low cost, high thermal stability, high proton mobility, water tolerance, recoverability and reusability [23]. Although HPAs are versatile compounds in their acidic form, their main disadvantages are high solubility in polar solvents and low surface area ($<10\,m^2/g$). Therefore, in a homogeneous reaction the isolation of the products and the reuse of the catalyst after reaction become difficult [23]. Therefore, in order to overcome this problem, these materials disperse on supports (such as silica, acidic ion-exchange resins, active carbon and etc.,) which possess large surface area. The use of support allows the heteropolyacids to be dispersed over a large surface area and increases their catalytic activity [24].

Recently, a number of functionalized Fe_3O_4 nanoparticles has been employed in a range of organic transformations, and the studies on immobilization of organo catalysts on silica coated ironoxide nanoparticles have been reported [25]. Therefore in this

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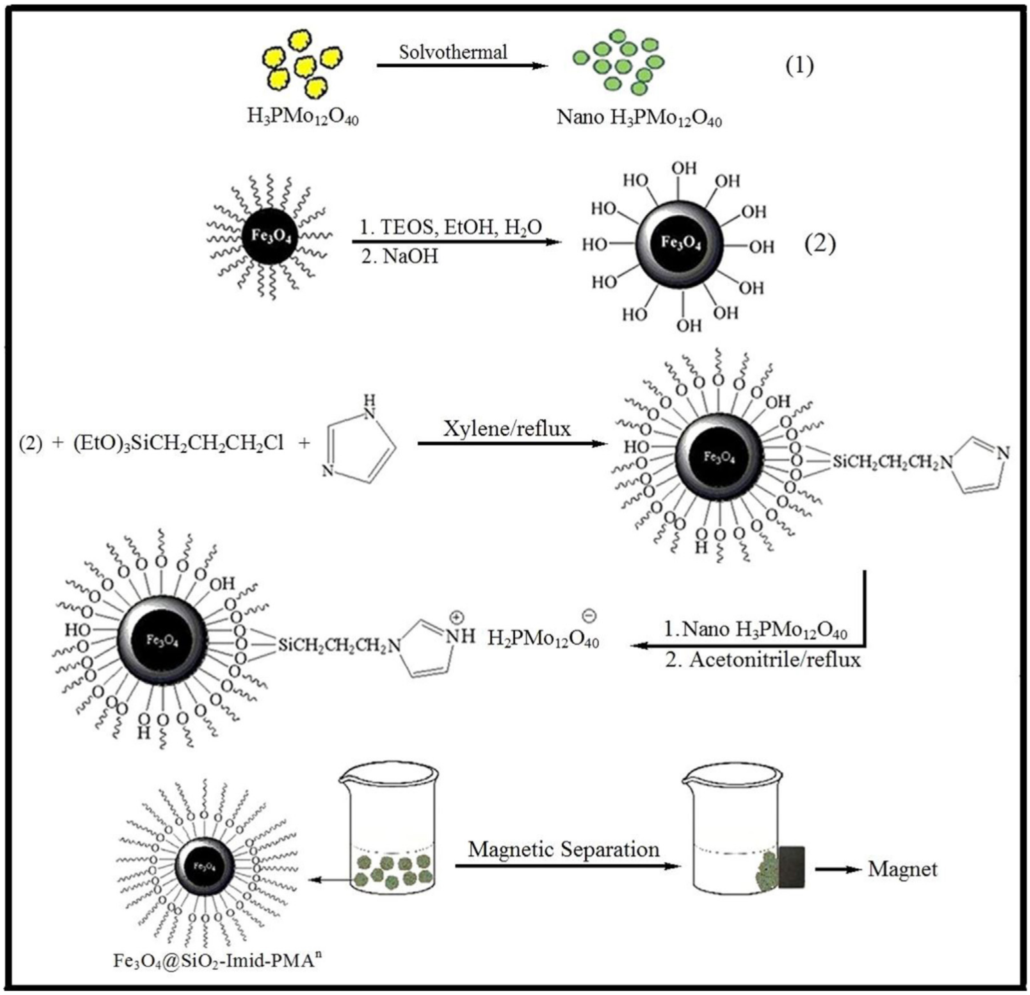

Scheme 1. Process for preparation of immobilization of $H_3PMo_{12}O_{40}$ nanoparticles (PMA^n) on imidazole functionalized $Fe_3O_4@SiO_2$ nanoparticle.

work, we report the immobilization of $H_3PMo_{12}O_{40}$ nanoparticles (PMA^n) on imidazole functionalized $Fe_3O_4@SiO_2$ as a convenient building block for the grafting of catalysts and reagents (Scheme 1).

Multicomponent reactions (MCRs) have attracted considerable attention in organic synthesis as they can produce the target products in a single operation without isolating the intermediates, thus reducing reaction times and energy consumption. MCRs have merits over conventional linear type syntheses in several aspects including simple procedures, possible structural variations, and rapid access to complex molecules [26]. Multi-component reactions (MCRs) play an important role in combinatorial chemistry because of their ability to synthesize small drug-like molecules with several degrees of structural diversity [27]. Therefore, discovery and development of new MCRs is highly desirable.

1-Amidoalkyl-2-naphthol derivatives are of prominence as they can be easily hydrolyzed to 1-aminoalkyl-2-naphthol. 1-Aminoalkyl-2-naphthols have been commonly applied as hypotensive and bradycardiac agents [28,29]. 1-Amidoalkyl-2-naphthols can also be converted to 1,3-oxazine derivatives [30] with different biological activities, such as antitumor [31], antibiotic [32], antipsychotic [33], anticonvulsant [34], antimalarial [35], analgesic [36], antihypertensive [37], antirheumatic [38], and antianginal [39] properties.

Therefore paying attention to the importance of amidoalkyl naphthols, various procedures have been reported. Many of these reported methods employ different homogeneous or heterogeneous catalysts such as *p*-toluenesulfonic acid [40], dodecylphosphonic acid (DPA) [41], H_2NSO_3H [42], oxalic acid [43], $Fe(HSO_4)_3$ [44], $Sr(OTf)_2$ [45], I_2 [46], $K_5CoW_{12}O_{40}\cdot 3H_2O$ [47], HPMo [48], $Yb(OTf)_3$ in ionic liquid [49], montmorillonite K10 [50], TMSCl/NaI [51], Al_2O_3–$HClO_4$ [52], $InCl_3$ [53], 2,4,6-trichloro-1,3,5-triazine [54], CuPW and CuPMo [55], $H_3MoO_{40}P$ [56], $H_4SiW_{12}O_{40}$ [57], and P_2O_5 [58]. However, most of the synthetic protocols for 1-amidoalkyl-2-naphthol reported so far suffer from drawbacks such as requiring reagents, which are not readily available, highly toxic and hazardous catalyst, unsatisfactory yields, long reaction times, use of harmful organic solvents and the production of environmental pollutants. Therefore, a great demand still exists for versatile, simple, and environmentally friendly processes whereby 1-amidoalkyl-2-naphthols may be formed under simple and practical conditions.

Therefore, we utilized $H_3PMo_{12}O_{40}$ nanoparticles (PMA^n) on $Fe_3O_4@SiO_2$-imidazol nanoparticle in the production of 1-amidoalkyl 2-naphthols.

2. Experimental

2.1. Chemicals and instrumentation

All the chemical reagents used in our experiments were purchased from the Merck Chemical Company in high purity. All the solvents were distilled, dried and purified by standard procedures. Melting points were determined on a Mel-Temp apparatus. The NMR spectra were recorded on a Bruker avance DPX