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$Fe_3O_4@SiO_2$–imid–PMA^n magnetic porous nanosphere as recyclable catalyst for the green synthesis of quinoxaline derivatives at room temperature and study of their antifungal activities

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ABSTRACT

An efficient, simple, and green procedure for the synthesis of quinoxaline derivatives catalyzed by $Fe_3O_4@SiO_2$–imid–PMA^n nanoparticles at room temperature is described. This environmentally benign method provides several advantages such as mild reaction conditions, good to excellent yields, short reaction times, simple work-up and catalyst stability, easy preparation, heterogeneous nature and easy separation of the catalyst. Also, nanocatalyst can be easily recovered by a magnetic field and reused for the next reactions for at least 6 times without distinct deterioration in catalytic activity. SEM, BET, DLS and leaching of catalyst after each reaction cycle were investigated. Furthermore, antifungal activity of various derivatives against three phytopathogenic fungi (*Alternaria alternata*, *Pyricularia oryzae*, and *Alternaria brassicae*) was investigated.

1. Introduction

Quinoxalines are very important compounds due to their wide spectrum of biological activities behaving as anticancer [1], antiviral [2], antibacterial [3–5] and activity as kinase inhibitors [6]. Also, quinoxaline moieties have found applications in macro cyclic receptors [7], chemically controllable switches [8], building blocks in the synthesis of organic semiconductors [9], electroluminescent materials [10], organic semiconductors [11], dehydroannulenes [12], DNA cleaving agents [13], anti-inflammatory, anti-protozoal and anti-HIV [14,15]. The quinoxaline ring is also found in antibiotics such as echinomycin, leromycin and actinomycin [16–18].

Because of important applications of quinoxaline compounds in both medicinal and industrial fields, a number of protocols have been developed for the synthesis of quinoxaline derivatives. The condensation of amines with ketones has been used as a useful protocol for the synthesis of quinoxalines. For this transformation, several catalysts and reagents have been reported, including acetic acid [19], oxalic acid [20], sulfamic acid [21], $H_6P_2W_{18}O_{62}\cdot 24H_2O$ [22], $KHSO_4$ [23], Ni nanoparticles [24], iodine [25], gallium(III) triflate [26], montmorillonite K10 [27], polyanilinesulfate salt [28], ZrO_2/Ga_2O_3/MCM-41 [29] and ionic liquids [17].

In addition, solid phase synthesis [30], microwave [31], bicatalyzed (bismuth and copper) oxidative coupling of peroxides and ene-1,2-diamines [32] were also reported. However, the critical product isolation procedure, long reaction time and harsh conditions of the above mentioned methods, non-recoverable catalysts, highly toxic and hazardous catalyst, limit their use in sustainable chemistry. Thus, the development of a new procedure for the synthesis of quinoxaline derivatives is still a desirable goal.

Nanoparticles (NPs) have been a topic of intense research mainly because of their unique physical and chemical properties compared with their bulk counterparts [33].

Metal oxide nanoparticles, with their potential applications in the fields of physics, chemistry, biology, and medicine have attracted increasing research attention from the past decades because of their interesting physical and chemical properties [34]. Magnetic nanoparticles have been widely used in the immobilization of enzymes [35], bio-separation [36], biosensor [37], immunoassay [38], targeted drug delivery and hyperthermia [39], environmental analysis [40] and catalysis [41–46].

In the field of catalysis, superparamagnetic nanoparticles have been utilized as catalyst supports for organic transformations such as alcohol hydrogenation [47], olefin hydrogenation [48], olefin hydroformylation [49], Sonogashira and Carbonylative Sonogashira

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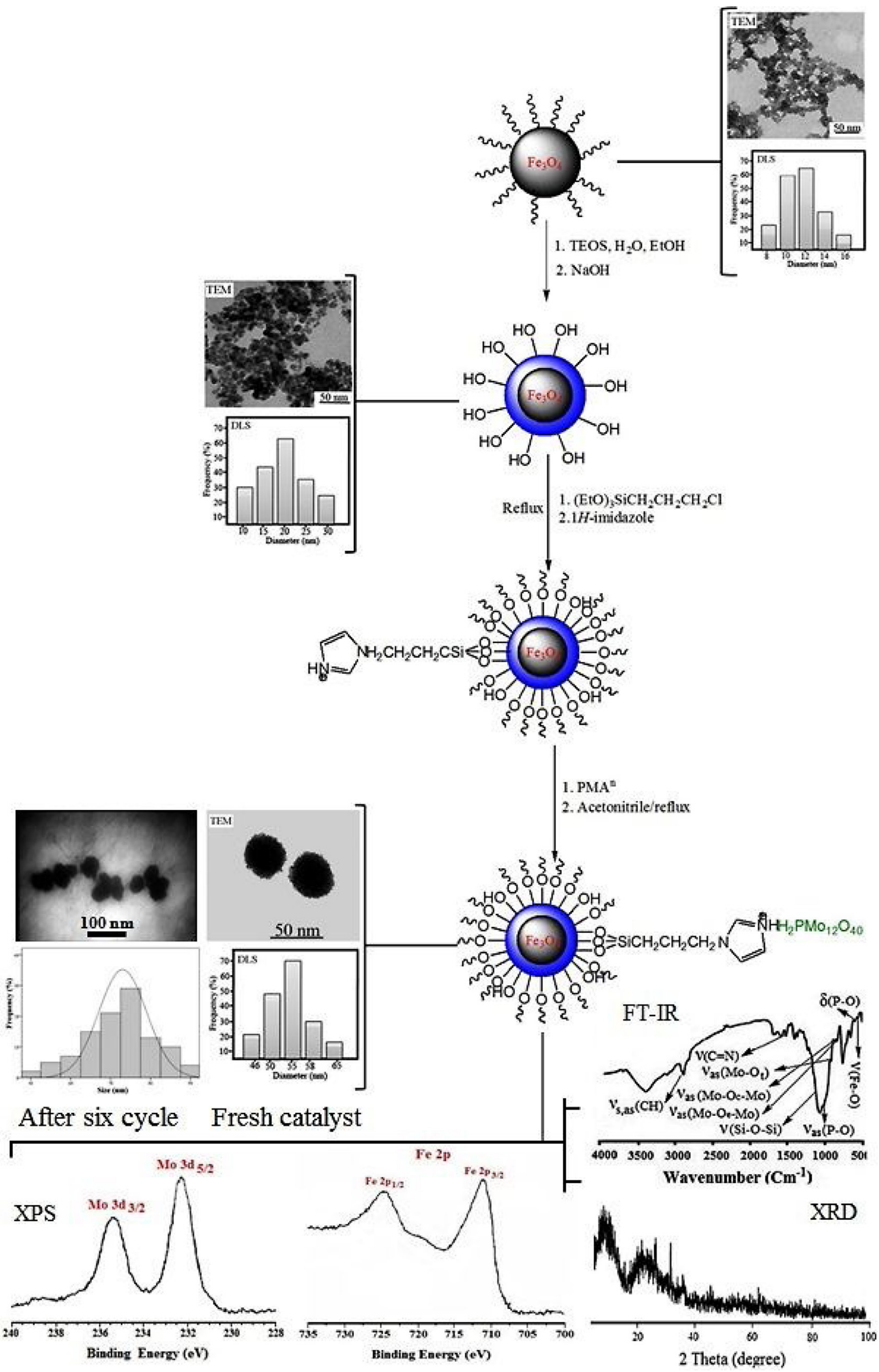
reactions [50], Suzuki and Heck cross-coupling reactions [51], oxidation [52], dehalogenation [53], ring-opening polymerization of epsilon-caprolactone [54], asymmetric hydrogenation [55], as well as supports for biocatalysts [56,57] with high activity and selectivity. Recently, a number of functionalized Fe_3O_4 nanoparticles have been employed in a range of organic transformations, and the studies on



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