



# Schiff base complex of metal ions supported on superparamagnetic Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles: An efficient, selective and recyclable catalyst for synthesis of 1,1-diacetates from aldehydes under solvent-free conditions

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## ABSTRACT

We report a new multistep method for preparing functionalized superparamagnetic Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> possessing high saturation magnetization. During the first step, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanosphere core-shell is synthesized using nano-Fe<sub>3</sub>O<sub>4</sub> as the core, TEOS as the silica source and PVA as the surfactant. Then, Schiff base complex of metal is synthesized from the reaction between Schiff base and metal acetates [Co(OAc)<sub>2</sub>, Mn(OAc)<sub>2</sub>, Ni(OAc)<sub>2</sub>, Cu(OAc)<sub>2</sub>, Hg(OAc)<sub>2</sub>, Cr(OAc)<sub>3</sub> and Cd(OAc)<sub>2</sub>] on the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> surface. The structural and magnetic properties of functionalized magnetic silica are identified by transmission electron microscopy (TEM) and vibrating sample magnetometer (VSM) instruments. Moreover, functionalized Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> possessed a superparamagnetic characteristic with saturation magnetization value of about 34 emu/g. NMR, FT-IR, elemental analysis and XRD were also used for the identification of these structures. The catalytic ability of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>/Schiff base complex of metal ions was found to be an efficient nanocatalyst for the conversion of aldehydes to their corresponding 1,1-diacetates compounds under mild and solvent-free conditions at room temperature. This method gives notable advantages such as excellent chemoselectivity, mild reaction condition, short reaction times and excellent yields. Also, the aforementioned nanocatalyst can be easily recovered by a magnetic field and reused for subsequent reactions for at least 5 times without noticeable deterioration in catalytic activity.

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## 1. Introduction

Nanoscale materials have been a subject of particular interest due to properties, which differ from their bulk counterparts [1]. They have been used extensively in chemistry [2], physics [3], biology [4] and catalysis [5]. Recently, magnetic core-shell nano-structures have attracted more attention due to their unique magnetic properties. In contrast to the difficulty observed in recovering and reusing most solid catalysts, core-shell nanostructure magnetic catalysts can be easily retrieved under the influence of a magnetic field and used in subsequent reactions. Due to this property, using magnetic core-shell structure composites as catalysts has been recommended in literature [6,7].

Magnetic metal oxides, in particular magnetite nanoparticles, were envisioned as magnetic storage media [8], contrast agents for magnetic resonance imaging (MRI) [9], for cancer treatment through hyperthermia [10] and a vessel for drug delivery [11].

Currently, much attention has been focused on the synthesis of magnetic metal oxide structures by coating a silica shell around a preformed nanoparticle [12–14].

Schiff base transition metal complexes have been extensively studied because of their potential use as catalysts in a wide range of reactions [15,16]. These complexes have been extensively used for hydrogenation of organic substrates [17], epoxidation of olefins [18], conversion of epoxides into halohydrines [19,20], asymmetric ring opening of terminal epoxides [21] and oxidation reactions [22,23].

Obviously, homogeneous catalysts show higher catalytic activities than their heterogeneous counterparts because of their solubility in reaction media, which increases catalytic site accessibility for the substrate [24,25]. However, recycling homogeneous catalysts, is often tedious and time consuming and there is also the issue of product contamination observed when these catalysts are used. Moreover homogeneous metal Schiff base complex catalysts are deactivated easily through the formation of dimeric peroxo- and  $\mu$ -oxo species [26,27]. For overcoming the aforementioned drawbacks, metal and organo catalysts are immobilized on silica coated Fe<sub>3</sub>O<sub>4</sub>. Recently, a number of such functionalized Fe<sub>3</sub>O<sub>4</sub>

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