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Nanocomposites with different metals as magnetically separable nanocatalysts for oxidation of aldehydes

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ABSTRACT

In this study, two metals were chosen for composing two different nanocatalysts. Zinc acetate and nickel chloride were used to prepare two nanocatalysts from acetanilide anchored to functionalized silica-coated Fe_3O_4 magnetic nanoparticles. They were identified using scanning electron microscopy, X-ray diffraction, Fourier transform infrared spectroscopy, and gas chromatography–mass spectrometry. These nanocatalysts were used for the oxidation of the following aldehydes: 3-hydroxybenzaldehyde, 4-methoxybenzaldehyde, and 3-nitrobenzaldehyde. High efficiency, stability, recoverability, recyclability, and selectivity were achieved using these nanocatalysts.

1. Introduction

Catalysts have a great effect on chemical reactions because they enhance the efficiency of reactions and decrease process temperatures [1]. Homogeneous catalyst particles dissolve easily in a reaction mixture, whereas heterogeneous catalyst particles do not [2]. High activity and good selectivity are benefits of homogeneous catalysts [3], as opposed to the restricted activity of heterogeneous catalysts. A major difficulty in processing of homogeneous catalysts is that after the reaction has completed, separation of the dissolved catalyst from the final mixture is difficult [4]. Unlike homogeneous catalysts, heterogeneous catalysts separate easily from the reaction mixture and thus do not cause product impurity [5]. Nanoparticles can be used to exploit both the high surface activity of homogeneous catalysts and the capability of separation of the catalyst at the end of the reaction found in heterogeneous catalysts [1]. Nanoparticles, especially metallic and metal oxide nanoparticles, are the most effective nanostructures for supporting catalysts [6]. Nanoparticles do not present a problem in recycling the used catalyst, but they do present a problem with separation of the catalyst from the reaction mixture. A proper technique for facilitating separation is magnetic separation [2]. Recently, magnetic nanoparticles (MNPs) have been broadly used as catalyst supports because of their highly active surface, which causes high loading capacity of the catalyst, high dispersion, remarkable stability, and ease of recovery [7]. Moreover, magnetic particles can withstand virtually all except highly acidic chemical environments. Because MNPs are highly susceptible to oxidation and agglomeration, they are best configured as a core–shell structure making use of either organic or inorganic shells [8]. Among different coatings, silica supports have the advantage of stability and inertness, facilitating functionalization, low cost, and high surface area [9]. The method of using metal–ligand grafting on silica-coated magnetite leads to higher loading than straight grafting of metals onto the same type of surface. Moreover, amine-functionalized nanoparticles have more catalytic activity than metal catalysts with silica coating. Among different metals, nickel and especially zinc are good choices because of their Lewis acid property, which helps the oxidation reaction [10]. Conventionally, oxidation has been performed without any catalyst by using an oxidant alongside mineral acids. This procedure is, however, harmful because it produces high amounts of dangerous wastes. To reduce this

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hazard to the environment, scientists have attempted to discover and enhance reactions that follow the doctrines of green chemistry [11]. The oxidation of aldehydes is a widely used reaction in organic chemistry [12]. Following the procedure used by Sharma and Monga [13], magnetite nanoparticles were coated with silica and then functionalized with (3-aminopropyl)triethoxysilane (APTES). Acetanilide was introduced to these particles, and finally zinc acetate and nickel chloride were used to prepare two different nanocatalysts. These were used for oxidation of aldehydes. Their easy separation from the reaction mixture was possible because of their magnetic characteristic [6].

High efficiency of the catalyst (with Zn as the metal) was exhibited. Significant conversion of different aldehydes to their acids was yielded (4-methoxybenzoic acid 98.3%, 3-nitrobenzoic acid 97.5%, and 3-hydroxybenzoic acid 97.2%) during the reactions performed under optimal conditions, even after six runs the magnetic nanocatalyst remained recyclable.

2. Materials and methods

2.1. Materials

APTES and tetraethyl orthosilicate were purchased from Merck, Germany. Hydrochloric acid (36.5%), acetanilide, zinc acetate, nickel chloride, ethanol, acetone, dichloromethane, acetonitrile, and hydrogen peroxide were obtained from Research Laboratory.

2.2. Characterizations

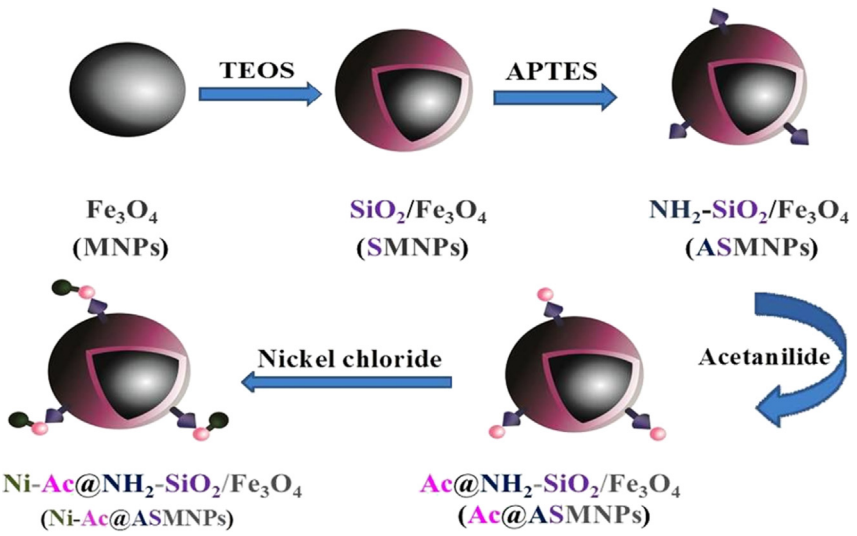
Perusal of nanocatalyst morphology was performed by scanning electron microscopy (SEM) on a KYKY-EM3200 scanning electron microscope. The phases of the products were assayed by X-ray diffraction (XRD) on a powder diffractometer using Cu Kα radiation ($\lambda = 1.54060$ Å) in the 2θ interval. Fourier transform infrared spectroscopy (FT-IR) were recorded using a Thermo Scientific Nicolet 8700 FT-IR spectrometer. The product of oxidation was analyzed and validated using gas chromatography–mass spectrometry (GC–MS).

2.3. Amino-functionalized SiO_2-coated Fe_3O_4 nanoparticle preparation

We prepared MNPs using a coprecipitation approach. To this end, we dissolved 6.0 g of ferric sulfate and 4.2 g of ferrous chloride in 250 mL of water and stirred the mixture at 60 °C to obtain an orange solution. Next, we subjoined 15 mL of ammonium hydroxide (25%) by stirring, which turned the color of the solution to black, and continued stirring for 30 min. We separated the MNPs and washed them with deionized water and ethanol. We carried out coating of the MNPs by the sol–gel method. We sonicated the solution of activated MNPs in 0.5 g of HCl (0.1 M) combined with 200 mL of ethanol and 50 mL of water, and then added 5 mL of ammonium hydroxide (25%) and 1 mL of tetraethyl orthosilicate to the suspension. We continued stirring at a temperature of 60 °C for 6 h. We separated the resulting SiO_2-coated MNPs (SMNPs) and washed them with ethanol. Finally, we sonicated 1.0 g of SMNPs in 700 mL of ethanol and charged the flask containing dispersed SMNPs with 5 mL of APTES, refluxing for 6 h at 80 °C to produce amino-functionalized SMNPs (ASMNPs). Separation and washing of the ASMNPs with ethanol were performed to remove the unreacted silylating agent.

2.4. Synthesis of Zn(II)–acetanilide complex anchored to ASMNPs

To anchor acetanilide onto the ASMNPs, we refluxed 3.0 g of ASMNPs and 6.0 mmol of acetanilide in 375 mL of ethanol at 80 °C for 3 h. To synthesize the nanocatalyst, we stirred 2.0 g of anchored ASMNPs in a solution of 8.0 mmol of zinc acetate in acetone for 4 h. Finally, we separated the



Scheme 1. Route for the synthesis of magnetic nanocatalyst with Ni as the metal.