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Novel magnetic nanomaterials: Synthesis, characterization and study of their catalytic application

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HIGHLIGHTS

- Designing an easy procedure for synthesis of magnetic heterogeneous catalysts.
- Anchoring of variety of Lewis acids on magnetic support.
- Synthesis of materials as environmentally friendly systems for catalytic reaction.
- Novel high-yield and selective catalysts for oxidation reaction.
- Recyclable catalysts with excellent reusability.

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ABSTRACT

A simple chemical process has been successfully developed to synthesize some N_2O_2 Schiff base metal complexes as an organic shell on an inorganic support. Schiff base complexes of Ni(II), Cu(II), Co(II) and Zn(II) were immobilized on modified magnetic support. The magnetic support was modified using tetraethylorthosilicate (TEOS) and then functionalized with Schiff base complexes of transition metals ions. The synthesized nanocatalysts show high catalytic activity and selectivity in the oxidation of sulfide compounds to corresponding sulfoxides. The hybrid nanomaterials were fully characterized with different physicochemical techniques including Fourier transform Infrared, X-ray diffraction analysis, thermal gravimeter, scanning electron microscopy and transmission electron microscopy. Also, magnetic properties of hybrid nanomaterials were measured by Alternative Gradient Field Magnetometer. Magnetic measurements showed that the coating of nanomaterials reduces the magnetization indicating modification of NPs with Schiff base complexes.

1. Introduction

Organic sulfoxides are considered as important intermediates in laboratory, industry and also are used as reagents in organic synthesis [1,2]. Besides, sulfoxides compounds are found in pharmaceutically active compounds [3]. It has been proved that the drugs such as cardiotonic, psychotonics and vasodilators using in therapeutic areas contain sulfoxide functionality [4]. Thus, based on this reality, chemoselective oxidation of sulfides to the corresponding sulfoxides has attracted lots of researcher's attentions during the past two decades [1,2].

To date, several methods have been reported for the synthesis of sulfoxides with different catalytic systems. These systems are based on titanium, copper [5] molybdenum [6] zinc [7] zirconium [8] and ruthenium [9] and so on.

Organic–inorganic Hybrid nanomaterials are combination of inorganic and organic components. Such materials are found in two forms: homogeneous form derived from monomers and inorganic and organic components, or heterogeneous form in which one of the components is in the range of nanometers [10]. Since the 1980s, hybrid nanocomposites had remarkable advances with the generalization of moderate inorganic chemistry processes. There are mild synthetic conditions such as sol–gel process involving low processing temperatures and metallo-organic precursors for combination of organic and inorganic components at the nanoscale [11,12].

During the last few years, hybrid materials have attracted a great deal of attention due to their critical role in the development of advanced functional materials [13–16].

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On the other hand catalysis is an important field in chemistry and industry. Also, more than 90% of chemical processes are run by catalysts and involved at least in one of the steps [17]. From the environmental point of view, catalysis is also more important than before and have an important role in the fabrication of the major sources of improvements [18,19].

In spite of high efficiency, the homogeneous catalysts have some drawbacks such as difficulty in separation and reuse of them. Thus, immobilization of homogeneous catalysts on these supports has attracted much attention. One easy method is to immobilize catalytically active materials on the surface of magnetic support that can be easily separated from the products and also recovered from the system by applying magnet [20–23]. One of the characteristics of superparamagnetic nanoparticles is that they are attracted to an external magnetic field. So, by using a magnet, magnetic nanoparticles can be easily removed from the system without any agglomeration [24].

In recent years, using of catalysts has been following by imposing an active organic species on a magnetic support in reactions such as asymmetric hydrogenation [24] olefin epoxidation [25], decarboxylative coupling [26] and hydrogenation reactions [27–29]. In metal coordination chemistry, Schiff-bases are one of the most widely used classes of ligands [30]. These ligands play an important role as chelating ligands in the main group and chemistry of transition metal coordination [31,32] because they have the capability of binding to the transition, non-transition, lanthanide and actinide metal ions to fabricate metal complexes with desired properties for practical applications [33]. Complexes of metal ions with Schiff base ligands have been playing a critical role in the progress of coordination chemistry due to their variation in structure and accessibility in preparation [34,35]. Among these complexes metal(II) Schiff-base complexes have attracted most of the researchers' attention due to their unique activities [36–38]. Also, these kinds of materials have attracted considerable interest in the synthesis and characterization of such complexes due to their important biological, catalytic and magnetic properties [39–42].

Recently, magnetic cobalt nanoparticles have attracted scientist's most attention. Zhuangjun et al. have reported the one step synthesis of cobalt nanoparticles in a graphitic shell [43]. In another report Francesca et al. have used cobalt nanoparticles for damaged skin [44]. Riffle et al. reported the cobalt–silica magnetic nanoparticles with functional surfaces with amines [45]. Wendelin et al. have reported the covalently functionalized cobalt nanoparticles as a platform for magnetic separations in organic synthesis [21].

Recently, some publication have been reported for sulfides oxidation using phthalazine-based diiron complexes [46], β-brominated meso-tetraphenylporphyrinatomanganese(III) acetate [47], Copper-Schiff base complex [48], immobilized metalloporphyrins [49], TsOH by phenyliodine diacetate as an oxidant [50], dendritic bis(acylamino)pyridines [51], $PyHBr_3/TBN/H_2O$ [52], MWW-type titanosilicate zeolite [53] and ruthenium porphyrins with iodobenzene diacetate [54].

Herein, we represent preparation and characterization of novel hybrid materials based on the interaction of silica coated magnetic cobalt nanoparticles with Schiff base complexes. On the other hand, due to the magnetic properties of cobalt core, the prepared hybrid nanomaterials are easily separable from the solution. So, they can be applied as magnetically recoverable catalysts.

To the best of our knowledge, this is the first report of immobilizing Schiff base complexes on the magnetic cobalt nanoparticles as a catalyst for the oxidation of sulfide compounds. Also, these hybrid materials have been used as highly efficient catalysts in the oxidation of alcohols [55].

2. Experimental and methods

All reagents and solvents were commercially available and purchased from Aldrich and used as received without further purifications.

2.1. Synthesis of magnetic cobalt nanoparticles

By a modified method [56], 1 g of cobalt chloride was dissolved in 60 ml doubly distilled water. Then, 0.07 g citric acid as a stabilizing agent was added to the solution followed by argon bubbling into the solution for 2 min. In another beaker, 3 g sodium borhydride was dissolved in 100 ml water and dropwise added to the stock solution under argon bubbling. By adding $NaBH_4$, the color of the solution was changed to a dark black indicating the formation of cobalt nanoparticles.

2.2. Synthesis of magnetic $Co@SiO_2$ nanoparticles

A 200 ml ethanolic solution of 3APTES (200 μl) and TEOS (800 μl) was added to the solution containing magnetic cobalt nanoparticles under the argon bubbling. Then, the argon atmosphere was cut off and the solution stirred for 24 h. A puffy black precipitate was obtained at the bottom of the beaker. The produced magnetic powder was separated by magnet and washed several times with ethanol and water. The precipitate was dried at 50 °C in the oven.

2.3. Synthesis of Schiff base ligand

To synthesize an appropriate ligand to bind with the silica layer of the magnetic support and have capability of making complex with metal ion, equimolar amounts of salicylaldehyde and 3-aminopropyl-triethoxysaline (3APTES) was mixed as follows: 1 mmol of 3-aminopropyl-triethoxysilane added to 5 ml methanol. (A). In another beaker 1 mmol salicylaldehyde was added to 5 mmol methanol (B). Then solution A and B mixed together and stirred for 30 min. A yellow solution was obtained that is indicative of formation of imine bond in Schiff base.

2.4. Synthesis of Schiff base complexes of metal (II) ions

2.4.1. Synthesis of Schiff base complex of cobalt

To synthesize cobalt (II) complex of Schiff base methanolic solution cobalt (II) acetylacetonate (1 mmol) was added to 5 ml methanolic solution of the Schiff base ligand. The total volume was reached to 40 ml and the mixture was refluxed for an hour. At the end of the reaction a light green precipitate was obtained at the bottom of the flask. The precipitate was washed with water and methanol and dried in the oven for further use.

2.4.2. Synthesis of Schiff base complex of nickel

In a typical procedure, a methanolic solution of nickel (II) acetylacetonate (1 mmol) was added to 5 ml methanolic solution of Schiff base ligand and the total volume was reached to 40 ml. Then the mixture was refluxed for an hour to complete the reaction. The synthesized precipitate was washed with water and methanol and dried in the oven.

2.4.3. Synthesis of Schiff base complex of zinc

A same procedure was carried out with zinc (II) acetylacetonate $Zn(acac)_2$. At the end of the reaction a yellow precipitate was obtained. The product was washed with water and methanol and dried in the oven for further use.

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