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Synthesis and characterization of heteropolytungstate-ionic liquid supported on the surface of silica coated magnetite nanoparticles

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ABSTRACT

Silica coated magnetic nanoparticles supported ionic liquid, IL-SCMNPs, was prepared by covalent attachment of chloropropyl silyl groups and reacted with 1-methyl imidazole on the surface of the silica coated magnetic nanoparticles. Then, reaction of IL-SCMNPs with $H_3PW_{12}O_{40}$ resulted in the preparation of heteropolytungstate-ionic liquid supported on the surface of silica coated magnetite nanoparticles, PW-IL-SCMNPs. The PW-IL-SCMNPs were characterized with different physicochemical methods such as Fourier transform Infrared and atomic absorption spectroscopies, X-ray diffraction, scanning electron microscopy (SEM), transmission electron microscopy (TEM), vibrating sample magnetometry (VSM), and thermogravimetric analyses. VSM analysis showed superparamagnetic properties of the materials and TEM and SEM analyses indicated the relatively uniform spherical nanoparticles with 20 nm average size. Finally, catalytic activity of the prepared PW-IL-SCMNPs was examined in the epoxidation of olefins with H_2O_2.

1. Introduction

Room temperature ionic liquids (RTILs) are generally composed of organic cations and inorganic anions and are liquids at room temperature. They have been shown to be suitable reaction media for synthesis [1–4], catalysis [5–9], electrochemistry [10,11], separation and extraction [12–14], chromatography [15,16], enzyme immobilization [17,18], etc.

On the other hand, immobilization of ionic liquids on the surface of solid supports offers the advantage of high surface area, facile recycling, and reuse. A number of methods have been reported for the preparation of supported ionic liquids [19–23]. Among them, covalent attachment via a spacer group to the surface of various solid supports is of great interests. Magnetic nanoparticles which have recently appeared as a new type of catalyst supports because of their good stability, easy synthesis and facile separation by magnetic fields have been used to immobilize ionic liquids [18,24].

Pure heteropoly acids have high solubility in polar reaction systems which hinder their application as heterogeneous catalysts and so make their separation problematic (results in separation problems). Water insoluble compounds of polyoxometalates with large cations such as Cs^+, K^+, NH_4^+ and organic cations can be used as efficient heterogeneous catalysts [25] and in recent years many efforts have been focused on the preparation and investigation of functional hybrid materials of polyoxometalates [25–29]. These compounds are prepared by partial or complete exchange of protons of heteropolyacids with the cations.

Though there are some reports about preparation of supported ionic liquid-poly oxometalate hybrid materials [28,29], to the best of our knowledge, there is no any report on the utilization of the ionic liquids supported on the surface of the magnetite nanoparticles for immobilization of polyoxometalates. Herein, we wish to report preparation and characterization of a new nanomaterial based on the interaction of ionic liquid modified silica coated magnetite nanoparticles with Keggin type polyoxometalate i.e. $H_3PW_{12}O_{40}$. The advantages of the resulted system are relatively strong chemical interaction between produced heteropolyanion and imidazolium group immobilized on the surface of magnetite nanoparticles and easy separation and recycling due to the superparamagnetic property of the prepared nanomaterial. Thus, the prepared nanomaterial can act potentially as magnetically recoverable nanocatalyst in the oxidation of olefins and alcohols.

2. Experimental

2.1. Materials and instrumentation

All chemicals were purchased from Merck chemical company without further purification. $H_3PW_{12}O_{40}$ was prepared according to the literature method [25].

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Fourier transform infrared spectra were recorded using Perkin–Elmer Spectrum RXI FT-IR spectrometer, using pellets of the nanomaterials diluted with KBr. The crystalline phase of the nanoparticles were identified by means of X-ray diffraction measurements using Cu kα radiation ($\lambda = 1.54$ Å) on a SIEFERT XRD 3003 PTS diffractometer in the 2θ range of 10–80°. Chemical analyses of the samples were carried out with VARIAN VISTA-MPX ICP-AES atomic absorption spectrometer. Magnetic susceptibility measurements were carried out using a vibrating sample magnetometer (BHV-55, Riken, Japan) in the magnetic field range of −8000 Oe to 8000 Oe at room temperature. The transmission electron micrographs (TEM) of the nanoparticles were recorded using a Philips EM 208S instrument with an accelerating voltage of 100 kV. Samples were prepared for TEM by placing droplets of a suspension of the sample in acetone on a polymer microgrid supported on a Cu grid. Scanning electron micrographs (SEM) of the samples were taken with ZEISS-DSM 960A microscope with an attached camera.

2.1.1. Preparation of ionic liquid modified silica coated magnetite nanoparticles (IL-SCMNPs)

Silica coated magnetite nanoparticles (SCMNPs) were prepared according to the reported method [30]. The obtained SCMNPs (2 g) were suspended in ethanol (100 ml) and then chloropropyl trimethoxysilane (2 ml) was added under dry nitrogen atmosphere. The mixture was refluxed for 12 h and the resulted solid was magnetically separated, washed with ethanol several times to remove the unreacted residue of silylating reagent and then vacuum dried at 80 °C. For the preparation of ionic liquid modified SCMNPs, ClpSCMNPs (2 g) was suspended in 100 ml of acetonitrile by sonication. To this mixture was added excess of 1-methyl imidazole (0.33 g, 4 mmol) and triethylamine (0.5 ml) and the resulted mixture was refluxed for 24 h. The resultant solid was separated magnetically and then washed with ethanol several times to remove the unreacted residue of the 1-methyl imidazole and dried under vacuum at 80 °C.

2.1.2. Preparation of heteropolytungstate-ionic liquid modified SCMNPs (PW-IL-SCMNPs)

First, the IL-SCMNPs (1 g) were dispersed in 50 ml deionized water in a 100 ml round-bottom flask with sonication. Then, a solution of $H_3PW_{12}O_{40}$ (2 mmol) in 20 ml deionized water was added to the above mixture and stirred for 12 h to yield PW-IL-SCMNPs. The products were magnetically separated and washed several times with deionized water and then dried under vacuum at 80 °C.

2.1.3. Catalytic epoxidation of cyclooctene in the presence of PW-IL-SCMNPs

Epoxidation of cyclooctene (purchased from Merck) was carried out in a 25 ml round bottomed flask equipped with a condenser and a magnetic stirrer. In a typical procedure, to a mixture of catalyst (100 mg) and cyclooctene (8 mmol) in acetonitrile (10 ml) H_2O_2 (1.6 ml) was added under nitrogen atmosphere and the mixture was refluxed for appropriate time. Samples were withdrawn periodically and after dilution with chloroform and cooling were analyzed using a gas chromatograph (HP, Agilent 6890N) equipped with a capillary column (HP-5) and a FID detector. Products were quantified using isooctane (1 g, 8.75 mmol, Merck) as internal standard. GC–MS of products were recorded using a Shimadzu-14A fitted with a capillary column (CBP5-M25).

3. Results and discussion

3.1. Preparation of heteropolytungstate-ionic liquid modified SCMNPs (PW-IL-SCMNPs)

The functionalization of magnetite nanoparticles with heteropolytungstate-ionic liquid was performed according to the sequence depicted in Fig. 1. First, the external surface of magnetite nanoparticles was silica coated to protect the magnetic nanoparticles from possible decomposition induced by the surrounding environment and also to prevent further aggregation. Treatment of silanol groups of

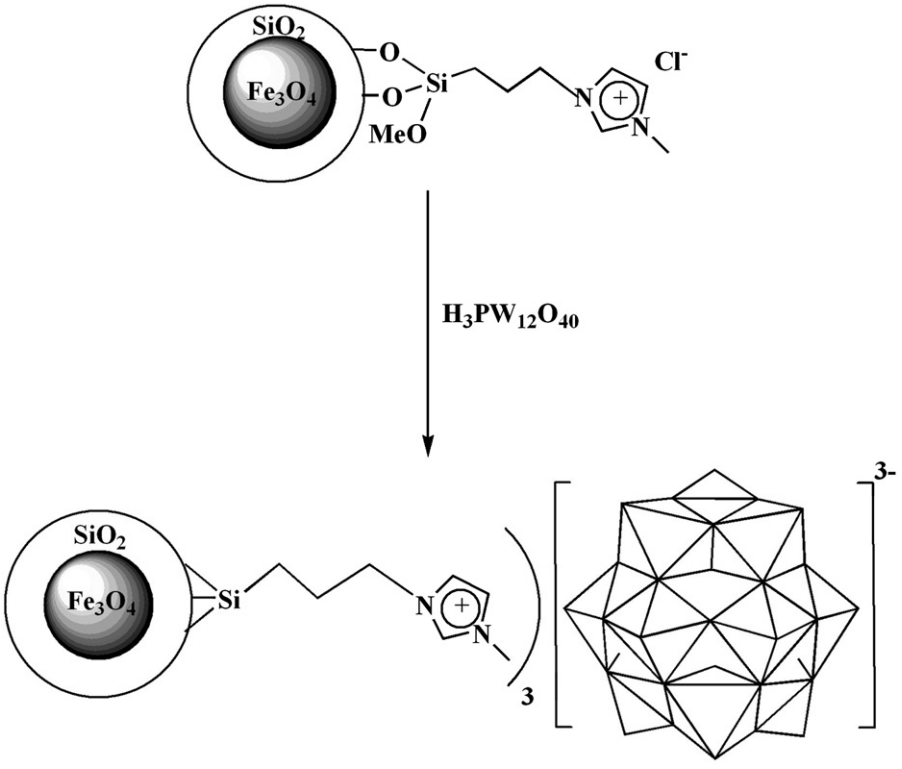

Fig. 1. Schematic illustration for preparation of PW-IL-SCMNPs.