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Novel high loaded magnetic nanocatalyst based on multi-layered coating of poly(1-vinylimidazole)

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HIGHLIGHTS

- A magnetic organocatalyst was synthesized.
- Fe_3O_4 was coated by cross linked poly(1-vinylimidazole).
- Catalyst has high loading level of homogenous catalytic functions.
- Catalyst was used for synthesis of 4*H*-benzo[*b*]pyrans in water.
- Catalyst was recycled ten times without any significant loss of catalyst activity.

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ABSTRACT

A novel magnetic catalyst was synthesized by the covalent grafting of poly(1-vinylimidazole) onto the surface of Fe_3O_4 (MNP@PVIm). The resulted catalyst was used in the synthesis of 4*H*-benzo[*b*]pyrans by three-component reaction under aqueous condition and the products were obtained in excellent yields. The catalyst showed appropriate thermal stability and excellent recyclability. Because of the multi-layered form of coated polymer, the catalyst has high loading level of imidazole groups and is used in the low weight percent, comparing to substrates. After completion of reaction, catalyst is recovered in a green way using an external magnet.

1. Introduction

In the last decades, heterogeneous catalysts have received much more attention than homogenous ones and many attempts have been done to combine the advantages of both. Homogenous catalysts are more effective than heterogeneous ones, while heterogeneous catalysts have the advantage of easy separation. A reasonable approach to combine these benefits is immobilization of homogenous catalysts on suitable solid supports. Many types of solid supports such as silica [1–3], polymers [4–6] and magnetic nanoparticles [7–9] have been used to heterogenize the homogenous catalysts. However, these immobilized heterogeneous catalysts solve separation and recyclability problems but they also have some unsolved disadvantages including low catalyst activity, low catalyst loading, high cost for large scale preparation, and need for environmentally hazardous organic solvents for purification of catalyst or reaction solvent.

Among the various supporting materials, magnetic nanoparticles are more interesting due to their magnetic response which causes easy separation of catalyst using a conventional magnet. Several organic and inorganic species have been immobilized onto the magnetic nanoparticles and utilized in various organic transformations [10–16]. However magnetic nanoparticles tend to aggregation, but it was found that coating of magnetic nanoparticles by polymer shells could help to improve the stability of nanoparticles [17–19].

The major problems of most immobilized heterogeneous catalysts are the low loading amount of immobilized catalyst and high catalyst leaching. In conventional immobilization of homogenous catalysts only one layer of surface is available for coating and therefore the loading amount is expected to be low. This problem could be solved by coating of solid surfaces by polymers [20–22]. Three different forms of polymers can be grafted onto the support surface including brush form [23], dendritic form [24], and multi-layered form [9,25]. In all of these protocols, the loading level of

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homogenous units on solid surface increases. Generally, the thermal stability and catalyst leaching improved in the multi-layered forms because in brush and dendritic forms the polymer chains are still attached to surface by one covalent bond for each polymer chain.

Herein, we report a novel magnetic heterogeneous basic catalyst which magnetic nanoparticles are coated by multi-layers of poly(1-vinylimidazole). The resulted magnetic catalyst was used in the synthesis of 4*H*-benzo[*b*]pyrans in aqueous medium. 4*H*-benzo[*b*]pyrans compounds have considerable attention as an important heterocyclic compounds because of their wide range of biological properties such as anti-cancer, anti-coagulant and anti-anaphylactic activates [26–28]. The conventional method for the synthesis of 4*H*-benzo[*b*]pyrans is using organic solvents such as DMF or acetic acid in reflux temperature which gives poor yields [29,30]. Several catalytic systems have been used for improving the yields of products [31–43], however most of these methods suffer from some disadvantages such as toxic reagents, long reaction times and no recyclability of catalysts and using toxic solvents. Therefore, to overcome these drawbacks a great deal of efforts is directed to develop an efficient catalyst for synthesis of these compounds in the green conditions.

2. Experimental section

2.1. General

Ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), ferrous chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$), 3-methacryloxypropyltrimethoxy-silane (MPS, 98%) and ammonia (30%) were obtained from Merck. 1-Vinylimidazole was obtained from Aldrich and distilled before use. 1,4-Dibromobutane was obtained from Aldrich. 2,2′-Azobisisobutyronitrile (AIBN) was purchased from Kanto and recrystallized from ethanol.

Thin layer chromatography (TLC) was performed with silica gel 60 F254 plates and UV light was used for Visualizatio. FT-IR Spectra of Samples were taken using an ABB Bomem MB-100 FT-IR spectrophotometer. The samples were powdered and mixed with KBr to make pellets. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Brucker NMR 500 MHz instrument in $CDCl_3$ or d_6-DMSO, and tetramethylsilane (TMS) was used as internal standard. Thermogravimetric analysis (TGA) was acquired under a nitrogen atmosphere with a TGA Q 50 thermogravimetric analyzer with heat rate 10 °C/min. Morphology of catalyst was observed by scanning electron microscope (SEM) instrument (Philips, XL30) after gold coating. Transmission electron microscopy (TEM) images were taken with a Philips EM 208 electron microscope operating at an accelerating voltage of 100 and 300 kV. The X-ray diffraction (XRD) pattern was recorded on a Rigalcu D/Max-3c X-ray diffractometer. The magnetic property of catalyst was measured by vibrating sample magnetometer (VSM) (Model 7400).

2.2. Synthesis of magnetic nanoparticles

The Fe_3O_4 magnetic nanoparticles were synthesized by a chemical co-precipitation method of ferric and ferrous ions in alkali solution. Typically, 13.60 g $FeCl_3{\cdot}6H_2O$ and 5.00 g $FeCl_2{\cdot}4H_2O$ were dissolved in 500 mL the deionized water. The mixture was stirred vigorously for 1 h at room temperature under N_2 atmosphere to form a homogeneous brown solution and then 100 mL ammonia solution 30% was dropwise added to the mixture. After the color of solution turned to black, the magnetite precipitates were magnetically separated and washed several times with deionized water.

2.3. Surface modification of magnetic nanoparticles

2 g Fe_3O_4 was suspended in 100 mL ethanol by ultrasonication for 20 min and then 4 mL ammonia solution 30% was added to the solution. Afterward, an excess amount of the 3-methacryloxypropyltrimethoxy-silane (MPS) (20 mmol per 1 g Fe_3O_4) was dropwise added over a period of 10 min, and the reaction mixture was stirred at 50 °C for 48 h. The flask was cooled down to room temperature and modified magnetic nanoparticles (Fe_3O_4@MPS) were magnetically separated and washed several times with methanol.

2.4. Synthesis of cross-linking agent 1,4-butanediyl-3,3′-bis-l-vinylimidazolium dibromide

2.82 g (30.0 mmol) 1-vinylimidazole, 3.24 g (15.0 mmol) 1,4-dibromobutane and 5 mL methanol were loaded into a 50 mL round bottom flask. The mixture was stirred at 60 °C for 15 h and then cooled to room temperature. The content of flask was dropwise added into 250 mL diethyl ether. The white precipitate of 1,4-butanediyl-3,3′-bis-l-vinylimidazolium dibromide (BVD) was filtered off and dried at room temperature in vacuum at 50 °C for 1 h (86% yields). ^{1}H NMR (DMSO, δ ppm): 2.13 (t, 2H), 2.44 (t, 2H), 4.34 (t, 2H), 5.40 (d, 1H), 5.95 (d, 1H), 7.29 (dd, 1H), 7.93 (s, 1H), 8.17 (s, 1H), 9.47 (s, 1H).

2.5. Synthesis of poly(1-vinylimidazole) coated magnetic nanoparticle

The magnetic MNP@PVIm was prepared by distillation–precipitation polymerization of 1-vinylimidazole and BVD as cross-linking agent and AIBN as initiator. Typically, 200 mg Fe_3O_4@MPS nanoparticles were ultrasonically suspended in 70 mL methanol for 20 min. Then, 500 mg 1-vinylimidazole and 200 mg BVD were added to flask and the mixture was completely deoxygenated by bubbling purified nitrogen for 30 min. Afterward, 2.5 mg AIBN was added to flask to initiate polymerization. The flask submerged in a heating oil bath was attached with a fractionating column, Liebig condenser, and a receiver. The reaction mixture was heated from ambient temperature to the boiling state within 1 h and the reaction was ended after about 45 mL methanol was slowly distilled from the reaction mixture within 6 h. The obtained MNP@PVIm was magnetically separated and washed three times with methanol to eliminate excess reactants and few generated polymer microspheres. The resulted MNP@PVIm was dried in vacuum at 50 °C for 2 h. The loading amount of basic imidazole groups on the surface catalyst was measured by back titration method. The resulting catalyst (0.1 g) was dispersed into 25 mL water and an excess HCl (0.1 M) was added to mixture to neutralization of

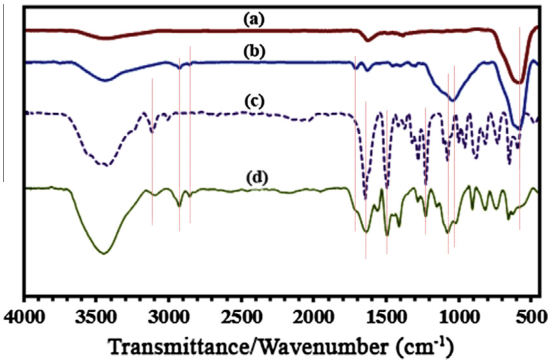

Fig. 1. FT-IR spectrum of (a) bare Fe_3O_4, (b) Fe_3O_4@MPS, (c) 1-vinylimidazole and (d) MNP@PVIm.