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Development of magnetically retrievable spinel nanoferrites as efficient catalysts for aminolysis of epoxides with amines

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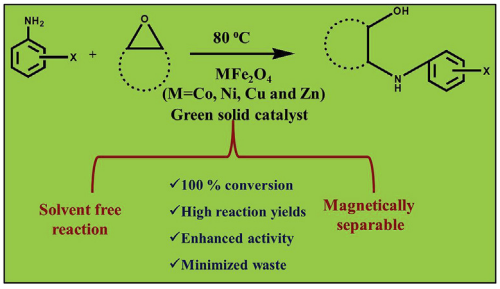
HIGHLIGHTS

- Spinel nano ferrites (M = Co, Ni, Cu and Zn) were successfully fabricated by different techniques.
- All the nanoferrites possessed small particle size, high surface area and good magnetic character.
- Catalytic activity was tested for epoxide ring opening reaction under solvent free conditions.
- $CoFe_2O_4$ nanoparticles synthesized hydrothermally were found to exhibit maximum activity.

GRAPHICAL ABSTRACT

Magnetically separable spinel nanoferrites as proficient green catalysts for epoxide ring opening reactions under solvent free conditions.



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ABSTRACT

Magnetically separable spinel nanoferrites (MFe_2O_4; M = Co, Ni, Cu and Zn) have been used as proficient catalysts for epoxide ring opening with amines. To study the effect of synthetic methodology on the catalytic activity, all the spinel nanoferrites were fabricated using three different techniques i.e sol-gel, hydrothermal and micro-emulsion method. The synthesized samples exhibited small particle size and high surface area values along with sufficiently magnetic nature to be used as magnetically separable heterogeneous green catalysts. The commencement of the important epoxide ring opening reaction via a green approach i.e by using magnetically recyclable nanoferrites under solvent free conditions in a very short reaction time (4–25 min), is the main highlight of the present work. Best catalytic results for epoxide ring opening were obtained with $CoFe_2O_4$ nanoparticles prepared using hydrothermal method which resulted in 100% conversion of the reactants to the corresponding amino alcohol.

1. Introduction

In recent years, green chemistry has gained great importance for the design of chemical processes that utilize environment friendly conditions to reduce or eliminate the generation of hazardous substances. Green chemistry involves various processes that can be potted as safer synthesis, safer products, renewable sources, catalysis, waste prevention, energy efficiency, degradability, pollution control and accident prevention [1]. The exploitation of solvent free reactions represents a unified effort towards the green chemical approach which not only

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solves the economic problems, but also reduces the burden of solvent disposal. Another greener feature involves the use of environmentally benign and recyclable magnetic nanocatalysts, which possess advantages such as low preparation cost, high activity, great selectivity, high stability, efficient recovery and good recyclability [2,3]. The major advantage of using magnetic nanocatalysts is their easy magnetic separation that prevents the loss of catalyst and enhances reusability.

Spinel ferrites are one such class of magnetic nanomaterials which have attracted a great deal of attention in the field of catalysis due to various interesting features such as smaller particle size, high stability, moderate saturation magnetization, easy separation and good recyclability [4–6]. Further, the structural flexibility of spinel ferrites allows easy modifications in their catalytic properties. The catalytic properties of spinel ferrites are greatly affected by change in the synthetic procedure. Various synthetic procedures such as sol-gel route [7], hydrothermal method [8], microemulsion technique [9], ball-mill method [10] have been employed by various researchers in order to change the particle size, morphology and overall the catalytic activity of the spinel ferrites. Various authors have reported the use of spinel ferrites as the catalysts in different organic reactions. Moghaddam et al. [11] have reported the synthesis of spinel ferrites (MFe_2O_4; M = Ni, Cu and Co) using co-precipitation method and compared their catalytic activities for the α-arylation of oxindole derivatives under the optimized reaction conditions. The catalysts allowed the α-arylation of different types of oxindole derivatives under mild conditions in very good yields and short reaction times. Jadhav et al. [12] have reported the synthesis of mesoporous zinc ferrite nanoparticles via co-precipitation method. The synthesized nanoparticles were then used for the synthesis of nopol by Prins condensation of β-pinene and para formaldehyde. The catalyst resulted in 70% conversion of β-pinene to nopol with 88% selectivity. The nanocatalyst was also found to be active towards other commercially important reactions such as isomerization, acetalization and aldol condensation. Sarode et al. [13] have reported the synthesis of copper ferrite nanoparticles via co-precipitation and thermal decomposition method. The nanoparticles were then used for the synthesis of 2-substituted benzoxazole by using one pot redox cascade condensation reaction of benzyl amine and 2-nitro phenol. The catalyst was reported to be highly active, air stable and recyclable upto six catalytic runs without any significant loss in activity.

Epoxide ring opening (ERO) is a very useful reaction as it offers a suitable route for the formation of C-C, C-N, C-S or C-O bonds. ERO is one of the key steps to synthesize polyketide skeleton, which are one of the most important organic intermediates for the synthesis of various organic compounds [14]. Though numerous reports are published for the epoxide ring opening using homogenous catalysts, very few reports are available for the epoxide ring opening using heterogeneous catalysts such as amberlyst-15 [15], hetropolyacid [16], zeolites [17], $BiCl_3$ [18], MCM-22 [19] and silica nanoparticles [20] etc. Hence, it is of great importance to develop such a heterogeneous catalyst, which can work in environment friendly conditions and also possess features such as facile magnetic separation and recyclability. Keeping in mind the advantages of spinel ferrites, the present work deals with the epoxide ring opening using spinel ferrites (MFe_2O_4; M = Co, Ni and Zn). Also, to study the effect of synthetic procedures on the catalytic properties of the catalysts, all the three ferrites have been synthesized using three different methodologies viz. sol-gel route, hydrothermal method and microemulsion technique. Keeping in mind the green chemistry approach, all the reactions have been performed under solvent free conditions at room temperature.

2. Experimental

2.1. Materials

Cobalt nitrate hexahydrate ($Co(NO_3)_2.6H_2O$), ferric nitrate ($Fe(NO_3)_3.9H_2O$), nickel nitrate ($Ni(NO_3)_2.6H_2O$), zinc nitrate ($Zn(NO_3)_2.6H_2O$), copper nitrate ($Cu(NO_3)_2.3H_2O$), sodium dodecyl sulfate (SDS) and sodium hydroxide (NaOH) were purchased from CDH chemicals. AR grade 1-Butanol, ethylene glycol and hexane were purchased from Avra chemicals and citric acid ($C_6H_8O_7$) was purchased from Fisher Scientific. All the obtained chemicals were then used as such without any further purification. Distilled water was obtained using an ultra-filtration system (Milli-Q, Milipore).

2.2. Synthesis processes

To study the effect of synthetic methodology on the catalytic properties, all the four metal ferrites (MFe_2O_4; M = Co, Ni, Cu and Zn) were fabricated using three different techniques i.e sol-gel method, hydrothermal technique and microemulsion route. The detailed synthetic procedure for the synthesis of spinel nanoferrites using different techniques is discussed below.

2.2.1. Synthesis of MFe_2O_4 via sol-gel approach

All the spinel nanoferrites (MFe_2O_4; M = Co, Ni, Cu and Zn) were prepared by dissolving metal salt, ferric nitrate and citric acid separately in minimum amount of deionized water in 1:1 M ratio. The solutions were thoroughly mixed and dissolved with continuous stirring and heating at about 80–90 °C. After that citric acid solution was added to the reaction mixture followed by addition of ethylene glycol (10 mL) to initiate gel formation. Resulting gels were dried and crushed to get ferrite powder [21]. The acquired ferrite powders were then subjected to annealing in a silica crucible for 2 h at 400 °C to acquire crystalline ferrites.

2.2.2. Synthesis of MFe_2O_4 via hydrothermal approach

In the hydrothermal method, all the spinel nanoferrites were prepared by dissolving the stoichiometric amounts of metal salt and ferric nitrate in minimum amount of distilled water. The pH of the solution was adjusted at 7.5 by addition of ammonia solution. The volume of the solution was made 120 mL by addition of distilled water followed by continuous stirring for 2 h. The solution was then transferred to a Teflon autoclave and treated hydrothermally at 160 °C for 15 h [22]. The precipitates were cooled down to room temperature and were thoroughly washed with distilled water and acetone. Finally, the obtained precipitates were dried in oven at 60 °C for 12 h.

2.2.3. Synthesis of MFe_2O_4 via microemulsion approach

In this method, two separate emulsions (I and II) were prepared using water: SDS: hexane: 1-butanol in appropriate weight ratios [23]. Both the emulsions were allowed to stir for 10–15 min. Stoichiometric amounts of metal salts and ferric nitrate were added to emulsion (I) and aqueous solution of 5 M NaOH was added to emulsion II. After continuous stirring for 15 min, both the emulsions were mixed slowly followed by continuous stirring for 1 h at room temperature. The obtained precipitates were thoroughly washed followed by drying in oven at 60 °C for 12 h. The dried precipitates were then finally annealed in silica crucible for 5 h at 400 °C.

2.3. Physical techniques

To confirm the formation of M-O bonds, Fourier transform infrared (FT-IR) spectra were recorded using iS50-FT-IR instrument (Model no. AUP1200343). Powder X-ray diffraction (XRD) analysis was performed using Panalytical's X'pert Pro diffractometer with diffraction angles of 10–80° in increments of 0.02° to explore the structural properties. The morphology of the synthesized ferrites was observed using field emission scanning electron microscopy (FE-SEM) instrument (Hitachi-SU8010). High resolution transmission electron microscopy (HR-TEM) images of ferrite powders were obtained using FEI Tecnai (G2 F20) instrument operated at an accelerating voltage of 200 keV. The magnetic studies of the samples were done using vibrating sample