



A magnetically recoverable nanocatalyst based on functionalized mesoporous silica



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ABSTRACT

A magnetically separable 2D-hexagonally ordered thiol functionalized mesoporous silica material (Fe@TFMS) has been synthesized through co-condensation reaction of 3-mercaptopropyltriethoxysilane (MPTES) and tetraethylorthosilicate (TEOS) using cetyltrimethylammonium bromide (CTAB) as a cationic surfactant followed by immobilization of Fe₃O₄ nanocrystallites at the functionalized mesopore surface. Powder X-ray diffraction (XRD), N₂ adsorption/desorption analysis, FT-IR, TEM, FE-SEM, TGA/DTA, CHNS, XPS and NH₃-TPD tools are employed to characterize the materials. This functionalized mesoporous material exhibited high catalytic activity in the biodiesel production from a wide range of long chain fatty acids and soybean oil. The material showed high Lewis acidity of 1.02 mmol g⁻¹ with a good Brunauer–Emmett–Teller (BET) surface area of 411 m² g⁻¹. Fe@TFMS exhibited excellent catalytic efficiency for this esterification reaction using methanol as a solvent cum reactant under eco-friendly and mild reaction conditions (room temperature, 25 °C).

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1. Introduction

In recent years biodiesel synthesis has attracted widespread interest in the context of future energy demand. Limited reserve of our natural fossil fuels, environmental degradation as a result of green-house gas emission from the burning of fossil fuels and other organic resources has prompted the demand of biodiesels [1]. Biodiesel is produced from the long chain fatty acids (animal fat and vegetable oil) through the esterification reaction with methanol/ethanol [2] and these compounds have huge potential as alternative resource to fossil fuels. The vegetable oil [3–5] and animal fats [6,7] are currently considered as the most attractive and easily available feedstocks for biodiesel production due to their lower market value in comparison with virgin oils. It is a sustainable, biodegradable, does not emit any hazardous and toxic compounds (green energy), suitable for use in the actual compression and ignition engine without any major purification, which could be produced very easily through acid or base-catalyzed esterification and transesterification reactions [8,9]. Various strategies

have been employed to overcome the common problems faced in the synthesis of biodiesels. Several insoluble solid acid catalysts like cation-exchange resin [10], combination of cation-anion exchange resin [11], phase transfer catalyst [12], mixed oxides [13], functionalized mesoporous silica [14], mesoporous carbon [15] and enzyme-immobilised magnetic support [16] etc. are utilized for the esterification reactions, substituting the homogeneous inorganic acid catalysts. However, efficiencies of many of the heterogeneous acid catalysts are quite unsatisfactory. For example zeolites showed poor catalytic efficiency due to the low densities and low accessibility of the acidic sites [17,18], whereas sulfated zirconia [19,20] does not have high BET surface area. Besides, these catalysts require high temperature reactivation. Further, diarryl ammonium incorporated catalyst support [21] although showed good catalytic activity it needs the use of expensive triflic acid, high temperature and pressure for the synthesis.

To fabricate a solid Lewis acid catalyst having good BET surface area substantial efforts have been devoted, but there are some intrinsic problems due to less accessibility of the active sites and enhanced diffusion limitation of reactant resulting in less catalytic activity and poor selectivity of the product. In recent years, the solid porous materials have been employed for biodiesel synthesis such as organically functionlized mesoporous silica material [22–24],

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metal organic frameworks (MOF) [25–27] and acid functionalized ionic liquids [28–30] etc. In most of the cases biodiesel is synthesized under drastic conditions [31], which is not eco-friendly. For the production of biofuel green synthetic pathways [32] are highly desirable to avoid those drastic conditions. There are only few reports for the biodiesel production at room temperature [33,34], though the main drawback of this reaction is the reversibility of the esterification reaction. Although Tang et al. have reported the Ca/Al/Fe₃O₄ magnetic composite as solid catalyst in the transesterification reaction [35] but the material has very poor BET surface area. On the other hand the magnetically recyclable ionic liquid immobilized mesoporous material FSS-IL can be used as an efficient catalyst for the esterification of oleic acid with ethanol for high biodiesel yield of 93.5% [36], but it requires elevated temperature for the reaction. During esterification reaction the product esters could be easily hydrolyzed in the presence of water molecule. To overcome this problem we have design a magnetically separable mesoporous heterogeneous catalyst, which can easily accommodate the water molecule from the reaction mixture, facilitating the esterification reaction at room temperature in the presence of minimum amount of methanol as a reagent and solvent.

Herein we report the synthesis of magnetically recoverable superparamagnetic Fe₃O₄ nanoparticle immobilized functionalized mesoporous silica having considerably high surface area with a tunable porosity and it displays excellent catalytic activity in the bio-diesel production at room temperature. Thiol functionalized mesoporous MCM-41 is prepared using 3-mercaptopropyltrimethoxysilane *via* co-condensation reaction. The reaction between thiol functionalized MCM-41 and dispersed Fe₃O₄ in absolute ethanol medium offers the formation of magnetically separable mesoporous material Fe@TFMS. The material has been characterized through PXRD, N₂ sorption, FESEM, XPS, FTIR spectroscopic tools, and displayed very easy product/catalyst recovery and good recycling efficiency without any loss of catalytic activity after five reaction cycles suggesting its future potential in large scale biodiesel production.

2. Experimental

2.1. Chemicals

Cetyltrimethylammonium bromide (CTAB), tetraethyl orthosilicate (TEOS) and (3-mercaptopropyl)triethoxysilane (MPTES, $M_{wt} = 196.34$ g/mol) were purchased from Sigma-Aldrich. Anhydrous ferrous chloride ($M_{wt} = 126.75$ g/mol) and ferric chloride ($M_{wt} = 162.20$ g/mol) was purchased from Merck, India. The solvents were used as received without further purification.

2.2. In-situ synthesis of thiol functionalized mesoporous silica (TFMS)

In a 100 mL cleaned plastic beaker 0.006 M (2.42 g) of CTAB was dissolved in 20 mL distilled water. This is followed by the addition of 0.02 M (4.166 g) tetraethylorthosilicate (TEOS) and 0.005 M (0.981 g) MPTES. The resulting white gel was allowed to stir for 15 min and then aqueous solution of NaOH was added dropwise to maintain the alkaline pH (11.7) conditions. The slurry was kept under static condition in polypropylene bottle at 75 °C temperature for 3 days. After the thermal treatment the white solid product was washed thoroughly with distilled water to get rid of extra template molecules (CTAB) and dried in air for 24 h. Then 0.5 g of as-synthesized solid product was subjected for acid-ethanol extraction to remove the template using 0.5 g of 1 N HCl and 20 mL absolute ethanol solution mixture for two times in each batch.

Finally, the extracted solid product was filtered by simple filtration technique and washed with distilled water for several times.

2.3. Synthesis of Fe₃O₄ nanoparticles

2.86 g (0.017 mol) of anhydrous FeCl₃ and 1.057 g (0.008 mol) of anhydrous FeCl₂ was dissolved in 60 mL distilled water taken in a 50 mL round bottom flask under inert atmospheric conditions. Then the reaction mixture was allowed to keep in a pre-heated oil bath at 80–85 °C temperature for 2 h after drop wise addition of aqueous ammonia (25%) to it. The resulting black precipitate was collected through filtration and washed with distilled water for several times to neutralize it. The black coloured solid product was dried in oven at 75 °C temperature for about 2 h.

2.4. Synthesis of Fe₃O₄ immobilized thiol functionalized mesoporous silica (Fe@TFMS)

The thiol functionalized MCM-41 was dispersed into a cleaned 100 mL glass beaker containing 25 mL absolute ethanol. Then, the brown coloured ethanolic suspension of Fe₃O₄ (0.1 g in 100 mL distilled water) was added drop by drop to the former solution and the solution mixture was stirred continuously for 12 h at room temperature. The resulting dark brown coloured solid product was filtered, washed thoroughly with ethanol and dried in air for overnight. The schematic representation for the formation of Fe₃O₄ nanoparticle grafted thiol-functionalized MCM-41 material (Fe@TFMS) is shown in Scheme 1 step by step. Here the thiol functionalized MCM-41 material (TFMS) has been synthesized by co-condensation of organosilanes in the presence of CTAB under hydrothermal conditions. This is followed by the removal of the template and impregnation of Fe₃O₄ NPs at the surface of TFMS to obtain magnetic nanocatalyst Fe@TFMS.

3. Characterization techniques

Nitrogen adsorption/desorption isotherms were obtained by using a Quantachrome Autosorb 1-C surface area analyzer at 77 K. Prior to gas adsorption, samples were degassed for 10–12 h at 453 K under high vacuum analysis. NLDFT theory was employed for pore size distributions measurement from the nitrogen sorption isotherm using the oxygen/cylindrical pore model. The powder X-ray diffraction patterns were recorded using Bruker D8 Advance SWAX diffractometer operated at voltage of 40 kV and current 40 mA. The instrument was calibrated with a standard silicon sample, using Ni-filtered Cu K α ($\lambda = 0.15406$ nm) radiation. FT-IR spectra of the functionalized mesoporous samples were recorded using a PerkinElmer spectrum 100 spectrophotometer. To analyse the morphology and particle size of the samples JEOL JEM 6700 field emission scanning electron microscope (FE SEM) was used. Transmission electron microscopic (TEM) images of the material were obtained using a JEOL JEM 2010 transmission electron microscope operating at 200 kV. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the sample were performed in a TGA instrument thermal analyzer TA-SDT Q-600 under air flow. The carbon, hydrogen, nitrogen and sulphur (CHNS) contents were determined in a Vario EL III elemental analysis analyzer. The temperature-programmed desorption of ammonia (NH₃-TPD) experiment was carried out on flow apparatus (Micrometrics TP-5080). The saturation magnetisation and magnetisation curve measurements were carried out using a 6 kOe vibrating sample magnetometer (VSM) at room temperature (RT).

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