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Full Length Article

Dehydration of glucose to 5-hydroxymethylfurfural by a core-shell Fe_3O_4@SiO_2-SO_3H magnetic nanoparticle catalyst[☆]

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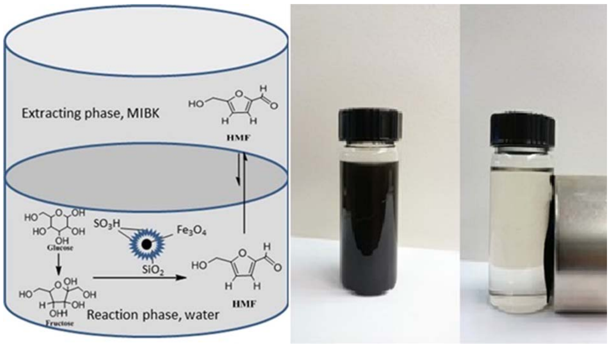
GRAPHICAL ABSTRACT



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ABSTRACT

In this paper we discuss the potential use of (Fe_3O_4@SiO_2-SO_3H) nanoparticle catalyst for the dehydration of glucose into 5-hydroxymethylfurfural (HMF). A magnetically recoverable (Fe_3O_4@SiO_2-SO_3H) nanoparticle catalyst was successfully prepared by supporting sulfonic acid groups (SO_3H) on the surface of silica-coated Fe_3O_4 nanoparticles. The prepared catalyst was characterized by FTIR, TGA, XRD, HRTEM-EDX, and N_2 adsorption-desorption isothermal analyses. The catalyst's surface acidity was determined by acid-base titration. Dehydration of glucose was performed in a biphasic system made up of water and methylisobutylketone (water/MIBK), and the effect of various reaction parameters affecting on the yield of HMF such as biphasic system ratio, catalyst concentration, temperature, time, and dimethylsulfoxide (DMSO) ratio were studied. Fe_3O_4@SiO_2-SO_3H catalyst disclosed a great catalytic activity for the formation of HMF and glucose conversion. About 70% yield of HMF and 98% glucose conversion were obtained at the optimum reaction conditions (40% catalyst concentration, 140 °C, 24 h and biphasic system of 1:4 (water: MIBK) ratio). At the end of the reaction, the catalyst was easily removed from the reaction mixture using a magnet and reused several times without high loss in catalytic activity.

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1. Introduction

Increasing energy demand and the existence of various problems associated with fossil fuels such as environmental pollution, global warming and diminishing petroleum reserves have greatly stimulated production of fuels and chemicals from renewable sources [1–3]. Lignocellulosic biomass has been considered as one of the potential sources for a variety of fuels and industrial chemicals [4,5]. HMF has been identified as an excellent platform molecule because it is a flexible intermediate for the synthesis of bio-renewable fuels and materials [6,7]. HMF can be converted to energy products such as 5-ethoxymethylfurfural [8], monomers for high-value polymers such as 2,5-furandicarboxylic acid [9], 2,5-hydroxymethylfuran [10]), and valuable intermediates for fine chemicals [11]. Therefore, extensive research about acid-catalyzed dehydration of carbohydrates to HMF has been performed [12–14].

Current feedstock resources of HMF production mainly includes cellulose, inulin, sucrose, glucose and fructose [15]. Some catalytic methods to produce HMF from glucose were reported in aqueous or organic media along with application of homogeneous and heterogeneous acids [16,17]. The use of organic solvents can provide many advantages and prohibit the formation of insoluble polymers and humins that can result from polymerization of carbohydrate degradation products. Also, the use of organic solvents can help to avoid the degradation of formed HMF into levulinic and formic acids as occurs in pure aqueous medium (acidified water) [18]. Dumesic and co-workers [6,19] have developed the use of biphasic reaction systems in which HMF formation can be enhanced in the aqueous phase (water) and simultaneously extracted by the organic solvent (organic phase). The use of biphasic system solves the problem of further conversion of produced HMF into undesirable levulinic or formic acid compounds through continuous extraction of furans into the organic phase. Biphasic solvents can also enhance the stabilization and yields of HMF product. Although heterogeneous catalysts are often recycled more easily than their homogeneous counterparts, the tedious recovery procedure via filtration or centrifugation and the inevitable loss of solid catalysts in the separation process still limited their application particularly for the small particle size.

Recently, magnetic nanoparticles based catalysts attracted more attention due to their good stability and easy separation from the reaction mixture by a permanent magnet [20,21]. The unique magnetic separation property makes MNPs much more effective than conventional filtration or centrifugation as it prevents loss of the catalyst. Several magnetic catalysts were successfully used for the conversion of biomass into chemicals and liquid fuels [22–24]. It has been demonstrated that the physical and chemical properties of the magnetic nanoparticles greatly depend upon the synthesis route [25]. To date, various techniques and different chemical synthetic methods for preparing magnetite (Fe_3O_4) nanoparticles (MNPs) already have been reported, such as co-precipitation, micro-emulsions, solvothermal processing, and high-temperature organic phase decomposition [26–28]. However, MNPs are readily aggregated due to electrostatic and magnetic attractions that can produce clusters. In order to prevent the aggregation, the surface of MNPs can be modified with various kinds of materials, including polymers [29], noble metals [30] and silica [31]. Among them, silica is considered to be one of the most promising candidates because it not only protects MNPs from oxidation and agglomeration, but it is also compatible with various chemicals and molecules for bio-conjugations due to its unique surface chemistry [32]. Currently, the Stöber method [33] and microemulsion method [34] are the most common approaches for silica coating. Zehui et al. prepared silica-coated MNPs supported phosphotungstic acid catalyst for the synthesis of 5-ethoxymethylfurfural from 5-hydroxymethylfurfural and fructose[35]. Zehui and his coworkers also used silica-coated MNPs supported sulfonic acid (SO_3H) catalyst successfully for the hydrolysis of cellulose in ionic liquids at low temperatures 70–100 °C [36]. It is well known that strong acid catalysts such as sulfuric or sulfonic acids can be used successfully for both hydrolysis and dehydration reactions. Wang et al. successfully used sulfonic acid-functionalized mesoporous carbon catalyst (OMC-SO_3H) for efficient conversion of fructose into 5-hydroxymethylfurfural and 5-ethoxymethylfurfural [37]. However, there was no previous studies discussed the ability of using silica coated MNPs supported sulfonic acid (SO_3H) as catalyst for the dehydration of sugars to furan derivatives. Due to the advantages of both magnetic nanoparticles acid catalysts and biphasic system, the purpose of this research is to study the effectiveness of silica coated MNPs supported with sulfonic acid groups (Fe_3O_4@SiO_2-SO_3H) on the dehydaration of glucose to HMF. For this purpose, this catalyst was prepared by immobilization of sulfonic groups (SO_3H) on the surface of silica-coated magnetite (Fe_3O_4@SiO_2) nanoparticles. The prepared catalyst was characterized by FTIR, TGA, XRD, HRTEM-EDX, N_2 adsorption-desorption analyses, and acid base titration. The factors affecting on the yield of HMF such as time, temperature, solvent composition, catalyst loads, and dimethylsulfoxide (DMSO) ratio were also studied.

2. Experimental

2.1. Materials

Ferric chloride hexahydrate (≥99%), 1-octadecene (technical grade 90%), polyoxyethylene (5) nonylphenylether (Igepal CO-520), tetraethyl orthosilicate (TEOS, reagent grade 98%), Oleic acid (technical grade 90%), chlorosulfonic acid (99%), formic acid (reagent grade ≥ 95%), 5-hydroxymethylfurfural (HMF, 99%), anhydrous hexane (95%) and anhydrous sodium hydroxide (pellets ≥ 99%) were purchased from Sigma-Aldrich. Dimethyl sulfoxide (DMSO, 99.5%), cyclohexane, ammonium hydroxide (reagent grade 29% by weight), ethanol and methanol were purchased from Fischer Scientific. Methyl isobutyl ketone (MIBK 99.5%), heptane, acetonitrile for HPLC and sulfuric acid (extra pure 96%) were purchased from Acros. D-glucose (≥99%), fructose, and levulinic acid were obtained from Alfa Aesar. High purity water (17.8 megohm-cm) was purified through Thermo Scientific E-pure Water purification system. All chemicals were used as-received without further purification.

2.2. Preparation of the catalyst

2.2.1. Preparation of Fe_3O_4 NPs

Fe_3O_4 NPs were synthesized according to the method described by Park et al. [38]. In a typical preparation procedure, 10.8 g of ferric chloride hexahydrate were dissolved in a solvent mixture composed of 120 mL deionized water, 160 mL ethanol, and 280 mL hexane. Then 38 mL oleic acid were added to the previously prepared solution and stirred at room temperature for 30 min. 4.8 g sodium hydroxide were added to the resulting solution and stirred in a closed reactor at 70 °C for 4 h. By using a separating funnel, the formed solution was separated into two different layers. The upper organic layer containing ferric oleate complex was collected and washed three times with deionized water. After washing, hexane was evaporated off overnight at 80 °C. The sticky ferric oleate precursor was dispersed in 6.4 mL of oleic acid and 250 mL of 1-octadecene. The mixture was degassed with helium for 30 min at room temperature. The reactants were kept at 100 °C for one hour to remove the residual solvents before heating up to 320 °C, then, the temperature was kept at 320 °C for 2.5 h under helium flow. The solution was cooled to room temperature and precipitated by addition of excess ethanol, the precipitate was collected by centrifugation and the supernatant decanted. The isolated solid Fe_3O_4 NPs was re-dispersed in heptane and then precipitated with ethanol. The precipitation and re-dispersion process was repeated several times to purify the prepared iron oxide NPs and then dried overnight via vacuum drying.