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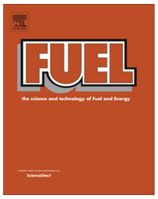

Efficient synthesis of promising liquid fuels 5-ethoxymethylfurfural from carbohydrates

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HIGHLIGHTS

- A new method was developed for the synthesis of 5-ethoxymethylfurfural (EMF).
- EMF was obtained in high yield of 88.4% from 5-hydroxymethylfurfural.
- EMF yields of 67.8% and 58.4% were obtained from fructose and inulin, respectively.
- The catalyst could be reused without the significant loss of its catalytic activity.

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ABSTRACT

In this study, we have developed an effective method for the conversion of carbohydrates into liquid biofuels 5-ethoxymethylfurfural (EMF) over a magnetic solid acid catalyst (Fe_3O_4@C—SO_3H). The as-prepared magnetic Fe_3O_4@C—SO_3H catalyst showed high catalytic activity toward the synthesis of EMF from carbohydrates. The etherification of 5-hydroxymethylfurfural (HMF) with ethanol over Fe_3O_4@C—SO_3H catalyst produced EMF with a high yield of 88.4%. The Fe_3O_4@C—SO_3H catalyst also showed high activity toward the one-pot conversion of fructose based carbohydrates into EMF. EMF was obtained in a yield of 67.8% from fructose, and that was 58.4% from inulin. The Fe_3O_4@C—SO_3H catalyst could be easily collected by an external magnet and reused for several times without the significant loss of its catalytic activity.

1. Introduction

The diminishing fossil reserves and environmental problems require our society to develop effective routes for the production of chemicals and fuels from renewable feedstocks [1–3]. Biomass, the only carbon-containing renewable resource, undoubtedly shows high potentiality as an alternative for the non-renewable fossil resources. Through biorefinery, biomass conversion can generate a variety of organic chemicals and liquid fuels [4–6].

5-Hydroxymethylfurfural (HMF) is considered to be a versatile intermediate between biomass- based carbohydrates chemistry and petroleum-based industrial organic chemistry [7,8]. It can be used to produce many value-added chemicals and liquid fuels, such as 2,5-furandicarboxylic acid, 2,5-diformylfuran and 2,5-dimethylfuran [9–11]. Due to the significant role in biorefinery, much effort has been devoted to the synthesis of HMF from carbohydrates in various catalytic systems [12,13].

5-Ethoxymethylfurfural (EMF), which is generated by the etherification of HMF, has been recently attracted considerable attention as a potential biofuel alternative [14]. EMF has a high energy density of 8.7 kW h/L, close to the standard gasoline (8.8 kW h/L) [15]. Currently, there were several methods on the synthesis of EMF. It is undoubted that the etherification of hydroxyl group in HMF with ethanol is the most effective way [16]. However, the practical large-scale synthesis of EMF from HMF is limited due to the high cost of HMF. As both the dehydration of fructose into HMF and the etherification of HMF into EMF are acid-catalyzed reactions, it is reasonable to integrate the two separable reactions into one-pot reaction. (Fig. S1). Homogenous acids generally showed high catalytic activity in one-pot conversion of fructose into EMF [17–19]. However, it is difficult to recycle homogeneous acids. Therefore, much effort has been focused on the development on the heterogeneous catalysts for the synthesis of EMF in order to overcome the problems of the homogeneous

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catalysts [20,21]. However, some heterogeneous catalysts showed low catalytic activity due to the weak acidity [21]. It is still required to develop new catalytic systems for the efficient conversion of carbohydrates into EMF.

Magnetic nanoparticles (MNPs) have recently appeared as a new type of catalyst support due to its magnetic separation properties. However, MNPs are readily aggregated due to the self interactions. Encapsulating magnetic cores with amorphous carbon shell not only protects the aggregation of the cores, but also the risk of erosion in an acidic environment [22]. In addition, the shell carbon materials can be functionalized with sulfonic acid groups (—SO_3H) to construct acid catalyst. Herein, we reported a feasible procedure to construct a new magnetic solid acid catalyst (Fe_3O_4@C—SO_3H) and used for the synthesis of EMF from carbohydrates.

2. Experimental section

2.1. Materials and method

$FeCl_3 \cdot 6H_2O$ (99.5%), polyvinylpyrrolidone (99.0%), ethylene glycol (99.0%), chlorosulfonic acid (99.5%), sodium acetate (99.0%), and ethanol (99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Fructose was purchased from Sanland-Chem International Inc. (Xiamen, China). Inulin and sucrose were purchased from the J&K Chemical Co. Ltd. (Beijing, China). 5-Hydroxymethylfurfural (98%) was purchased from Beijing Chemical Co. Ltd. (Beijing, China). 5-Ethoxymethylfurfural (98%) was purchased from Hangzhou Imaginechem Co., Ltd. (Zhejiang, China). Acetonitrile (HPLC grade) was purchased from Tedia Co. (Fairfield, USA).

2.2. Preparation of the catalyst

2.2.1. Synthesis of Fe_3O_4 nanoparticles

Fe_3O_4 nanoparticles were prepared according to the known method [23]. Briefly, $FeCl_3 \cdot 6H_2O$ (1.5 g), polyvinylpyrrolidone (1.0 g) and sodium acetate (2.0 g) were added into ethylene glycol (30 mL) in sequence, and the mixture was stirred vigorously for 2 h at room temperature to form a homogeneous solution. Then, the mixture was transferred into a Teflon-lined stainless-steel autoclave and sealed to heat at 200 °C for 8 h. The black precipitates were collected from the solution by an external magnet and washed with ethanol several times. Finally, the black Fe_3O_4 nanoparticles were dried in a vacuum oven for 24 h at 60 °C.

2.2.2. Synthesis of magnetic Fe_3O_4@C composites

The core–shell Fe_3O_4@C composites were synthesized by in situ carbonization of glucose under hydrothermal conditions [24]. Typically, glucose (6.0 g) was firstly dissolved in water (90 mL), and then Fe_3O_4 nanoparticles (300 mg) were dispersed in glucose solution with ultrasonic assistance. Then, the mixture was transferred to a Teflon-lined stainless-steel autoclave. The autoclave was heated at 200 °C for 12 h. then it was cooled down to room temperature. Fe_3O_4@C composites were collected by an external magnet and washed with water several times. Finally, Fe_3O_4@C composites were dried in a vacuum oven for 24 h at 60 °C.

2.2.3. Synthesis of magnetic Fe_3O_4@C—SO_3H catalyst

Sulfonation of Fe_3O_4@C material was carried out in a similar way for the sulfonation of hollow sphere carbon as reported by Wang et al. [25]. Fe_3O_4@C (0.5 g) composites were added into a solution of chlorosulfonic acid (0.3 mL) in dichloromethane (50 ml), and the mixture was stirred at room temperature overnight. Then, it was removed from the reaction solution by an external magnet, and washed with dichloromethane (50 ml), acetone (50 ml), and ethanol (50 ml) in sequence. Finally, it was dried at 70 °C for 24 h to obtain the sulfonic acid groups functionalized magnetic acid catalyst, which was abbreviated as Fe_3O_4@C—SO_3H.

2.3. Catalyst characterizations

Nitrogen adsorption isotherms were measured with an Autosorb-1 (Quantachrome, USA) at 77 K. Prior to the measurement, all the sample was degassed at 200 °C for 6 h in a vacuum line. The BET surface area was determined by a multipoint BET method 75 using the adsorption data in the relative pressure (P/P_0) range of 0.05–0.3.

Transmission electron microscope (TEM) images were obtained using an FEI Tecnai G^2-20 instrument. The sample powder were firstly dispersed in ethanol and dropped onto copper grids for observation. Fourier transform infrared (FT-IR) spectra were conducted on a Nicolet NEXUS-6700 FTIR spectrometer with a spectral resolution of 4 cm^{-1} in the wave number range of 500–4000 cm^{-1}. X-ray powder diffraction (XRD) patterns of samples were determined with a Bruker advanced D8 powder diffractometer (Cu Kα). All XRD patterns were collected in the 2θ range of 10–80° with a scanning rate of 0.016 deg/s. The sulfur content was conducted on a 2400 Series II CHNS/O Elemental Analyzer (Perkin Elmer). The amount of H^+ in the Fe_3O_4@C—SO_3H was determined by acid–base titration. Before the titration, the Fe_3O_4@C—SO_3H sample was stirred variously in 0.1 M NaCl solution to exchange the H^+ in the catalyst by Na^+. Then the librated H_3O^+ was titrated by standard NaOH.

2.4. Synthesis of EMF from HMF

Typically, HMF (126 mg, 1 mmol), Fe_3O_4@C—SO_3H (100 mg) and ethanol (5 mL) were added into a 10 mL stainless steel vessel. The mixture was magnetically stirred at 600 revolutions per minute (rpm) and 100 °C. Small aliquots were withdrawn from the reaction mixture at a given reaction time, and diluted with deionized water to a certain concentration for HPLC detective range.

2.5. Synthesis of HMF from fructose based carbohydrates

Typically, fructose (1 mmol, 180 mg), Fe_3O_4@C—SO_3H (100 mg) and ethanol (5 mL) were added into a 10 mL stainless steel vessel. Then the reaction was carried out at 100 °C. Other steps were the same as those described above.

When using inulin as the starting material for the synthesis of EMF, 162 mg of inulin was used, which equaled to 1 mol of fructose unit. Inulin (162 mg), Fe_3O_4@C—SO_3H (100 mg) and ethanol (5 mL) were added into a 10 mL stainless steel vessel. The reaction was carried out at 140 °C for the desired reaction time. Other steps were the same as those described above.

2.6. Analytic methods

The amounts of HMF and EMF were analyzed on a ProStar 210 HPLC system equipped with a UV detector. HMF and EMF could be well separated by a reversed-phase C18 column (200 × 4.6 mm) with a detection wavelength of 280 nm. The mobile phase was composed of acetonitrile and 0.1 wt.% acetic acid aqueous solution at the volume ratio of 15:85, and the flow rate was set at 1.0 mL/min. The column temperature was maintained at 25 °C. The content of HMF and EMF in samples were obtained directly by interpolation from calibration curves, with a coefficient of 0.999.

The content of fructose was analyzed by an aminex column HPX-87 column and Refractive Index detector.