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# Magnetically recyclable cellulose-derived carbonaceous solid acid catalyzed the biofuel 5-ethoxymethylfurfural synthesis from renewable carbohydrates

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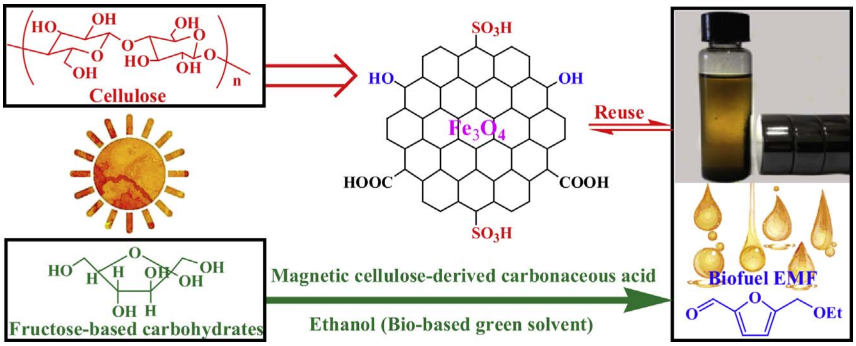
## GRAPHICAL ABSTRACT



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## ABSTRACT

A series of carbonaceous solid acid catalysts were prepared by facile carbonization and sulfonation of biorenewable feedstocks (i.e., glucose, sucrose, starch and cellulose), and employed for directly converting carbohydrates in ethanol medium to synthesize 5-ethoxymethylfurfural (EMF). The carbonization temperature of cellulose and starch (500 °C) was required to be higher than that of glucose and sucrose (400 °C) to realize high $–SO_3H$ density and EMF yield. Based on rich exploitability of cellulose and good activity of its derived carbonaceous catalyst, magnetic cellulose-derived carbonaceous solid acid (MCC-$SO_3H$) was subsequently synthesized, which possessed a porous structure with BET surface area of $35.34\,m^2\,g^{-1}$, high $–SO_3H$ density ($1.28\,mmol\,g^{-1}$) and sufficient magnetism for separation ($1.99\,emu\,g^{-1}$). By optimizing the process variables, a maximum EMF yield of 63.2% could be achieved from fructose at 120 °C, and ethyl levulinate formation was favored at elevated temperature. The MCC-$SO_3H$ catalyst could be readily separated from the reaction mixture by an external magnet with recovery rate of 92.6% after six successive runs, and reused repeatedly with little deactivation. Besides, this catalyst was efficient for the one-pot transformation of fructose-based polysaccharides into EMF, affording yields of 51.3% and 32.5% from inulin and sucrose, respectively. With glucose as the substrate, instead ethyl glucoside with a high yield of 86.5% was obtained.

## 1. Introduction

There is a growing interest in the exploitation of renewable resources to produce fuels and chemicals for our society due to the environmental pollution issue and diminishing fossil fuel reserve. Abundant available biomass, the only carbon-containing renewable resource on earth, is considered to be the most promising alternative source for the sustainable supply of liquid fuels and chemicals [1–4]. As

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an important biomass-based platform compound for plastics and fuels, the production of 5-hydroxymethylfurfural (HMF) by acid-catalyzed dehydration of carbohydrate that is the major component of biomass has been substantially studied [5–7]. Nowadays, 5-ethoxymethylfurfural (EMF), as one of the derivates of HMF, is receiving considerable attention purporting its potential use as a transportation fuel or biodiesel additive, owing to its superior prosperities including high energy density, low toxicity, good stability, and proper flow properties [8].

At present, EMF with high yields can be synthesized through the etherification of HMF [9–11]. However, it should be pointed out that the direct use of HMF as raw material is economically unfeasible because of HMF production having a relatively high cost. Obviously, it is much more attractive to employ renewable carbohydrates, such as fructose and glucose, as the starting materials for one-pot synthesis of EMF. Acid catalyst is identified as the key point for this reaction. To date, many acid catalysts have been proposed for the conversion of carbohydrates into EMF, including mineral acids [12,13], metal compounds [14–17], hydrogen sulfate ionic liquids [18,19], and solid acid catalysts, such as heteropolyacid [20,21] and its supported nanoparticles [22,23], acid-modified silica mesoporous materials [24,25], graphene oxide [26]. Most homogenous acids are inexpensive and effective, but they suffer from serious drawbacks in terms of separation and recycling, as well as equipment corrosion. Heterogeneous catalysts can overcome the above-mentioned disadvantages of homogenous catalysts to a certain extent. It is a litter pity that the tedious recovery procedure by filtration or centrifugation and the unavoidable loss of solid catalysts in the separation process still limits their practical application, particularly for nanoscale particles. For this, functionalized magnetic catalysts have emerged as viable alternatives to conventional heterogeneous catalysts due to their good stability, facile separation by an external magnetic force, and little loss in recycle runs [27,28]. Presently, there were several reports regarding the synthesis of EMF using magnetic solid acid catalysts, such as silica coated magnetic $Fe_3O_4$ nanoparticles supported phosphotungstic acid [29], sulfonic acid-functionalized silica-encapsulated $Fe_3O_4$ nanoparticles [30], and magnetic material grafted cross-linked imidazolium based polyionic liquids [31].

Compared with the above-mentioned solid acid catalysts, more environmental-benign and low-cost carbon-based solid acid catalysts, which are generally prepared by the incomplete carbonization of carbon-containing materials (e.g., glucose, starch, cellulose, lignin) and the subsequent sulfonation of the resulting amorphous carbon, have been identified as a novel class of solid acid catalysts in recent years and also widely used in the acid-catalyzed reactions [32–37]. Cellulose is the major component of lignocellulosic biomass, which is readily available and does not compete with the food supply, thus providing an excellent source for the preparation of carbonaceous solid acid catalyst with special characteristics. Herein, a magnetic cellulose-derived carbonaceous solid acid catalyst (MCC-$SO_3H$) was synthesized by a facile and inexpensive process involving impregnation, carbonization and sulfonation. For comparison, other biomass components including glucose, sucrose, and starch were also used as carrier materials to synthesize carbonaceous catalysts. The as-prepared catalysts were well characterized by several model technologies, and their catalytic activities were evaluated for the synthesis of EMF from fructose in ethanol medium. Subsequently, the effects of process variables, the recycling of catalyst and the feasibility for the conversion of other renewable carbohydrates into EMF were investigated in the presence of MCC-$SO_3H$ catalyst. To the best of our knowledge, this is the first report of the use of magnetic cellulose-derived carbonaceous solid acid as a readily recyclable and bio-supported catalyst for the synthesis of EMF.

## 2. Materials and methods

### 2.1. Materials

The chemicals including cellulose, starch, glucose, fructose, sucrose, inulin, 5-hydroxymethylfurfural (HMF), ethyl levulinate (EL), NaOH, NaCl, $FeCl_3{\cdot}6H_2O$, and $FeCl_2{\cdot}4H_2O$ were purchased from Aladdin Reagent (Shanghai, China). 5-Ethoxymethylfurfural (EMF) was obtained from Sigma-Aldrich (Shanghai, China). Ethyl glucoside (EGO) and ethyl fructoside (EFO) were provided by Chemsynlab Pharmaceutical Science & Technology Co., Ltd (Beijing, China). Ethanol, $NH_3{\cdot}H_2O$ (25–28%), $H_2SO_4$ (98%), and HCl (37%) were supplied by Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All reagents and chemicals used were of analytical grade and employed without further purification.

### 2.2. Catalyst preparation

#### 2.2.1. Synthesis of carbonaceous solid acid

Four biomass-based components including glucose, sucrose, starch and cellulose were selected as carrier materials of carbonaceous catalysts. In the preparation of catalyst, biomass sample was dried at 105 °C for 24 h, and heated at stated temperatures (400–600 °C) for 4 h under $N_2$ atmosphere to produce incompletely carbonized solid, which was grinded to a powder. The carbonized sample was impregnated in concentrated sulfuric acid with a solution/solid ratio of 20 mL/g and heated at 150 °C for 8 h with a mechanical stirring to introduce –$SO_3H$ groups. The obtained solid was washed thoroughly with hot-water (80 °C) to remove any physically adsorbed species until the pH value of washed water reached 7.0. The resulting sample was dried in an oven at 105 °C for 24 h to obtain carbonaceous solid acid catalyst. The prepared catalysts using glucose, sucrose, starch and cellulose as carrier materials were denoted as GC-$SO_3H$, SuC-$SO_3H$, StC-$SO_3H$, and CC-$SO_3H$, respectively. In later use, figures in brackets connected to the catalysts represent the carbonization temperature of raw materials. For example, CC-$SO_3H$ (500) meant that cellulose was carbonized at 500 °C.

#### 2.2.2. Synthesis of magnetic cellulose-derived carbonaceous solid acid

10 g cellulose was added into 80 mL aqueous solution of 2 g $FeCl_3{\cdot}6H_2O$ and 1 g $FeCl_2{\cdot}4H_2O$. Concentrated $NH_3{\cdot}H_2O$ was added dropwise to it to adjust the pH value of 10, and the mixture was continuously stirred at room temperature for 12 h. Then, the water in the mixture was evaporated and the remaining mixture was dried in an oven at 80 °C for 12 h. The resulting solid was calcined at 500 °C in a $N_2$ atmosphere for 4 h, and this material is denoted as magnetic cellulose-derived carbonaceous material (MCC). The next steps were the same as the preparation of CC-$SO_3H$ catalyst. Finally, magnetic cellulose-derived carbonaceous solid acid catalyst was obtained and labeled as MCC-$SO_3H$.

### 2.3. Catalyst characterization

The surface morphologies of catalysts was observed using a Hitachi S4800 scanning electron microscope (SEM). X-ray diffraction (XRD) patterns of the samples were carried out on a Rigaku D/MAX 2200 diffractometer with a Cu Kα radiation source operated at 40 kV and 100 mA. The functional groups of catalysts were detected by Nicolet 5700 Fourier transform infrared (FT-IR) spectroscopy using the standard KBr disc method over the wavenumber range of 400–4000 $cm^{-1}$ with a resolution of 2 $cm^{-1}$. X-ray photoelectron spectroscopy (XPS) analysis were made on a Thermo ESCALAB 250XI system employing an Al Kα radiation source. The magnetic properties of the samples were studied by using a Quantum Design MPMS SQUID XL magnetometer. The thermogravimetric analysis of catalysts were performed by a TA Instruments Q500 thermo gravimetric analyzer (TGA) under $N_2$ atmosphere with the temperature range of 30–800 °C at a heating rate of