



Full Length Article

Efficient conversion of carbohydrates into 5-hydroxymethylfurfan and 5-ethoxymethylfurfural over sulfonic acid-functionalized mesoporous carbon catalyst



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HIGHLIGHTS

- Sulfonic acid-functionalized mesoporous carbon (OMC-SO₃H) was prepared.
- It is an effective acid catalysts for the synthesis of HMF and EMF.
- A high HMF yield of 89.4% was obtained from fructose at 120 °C within 30 min.
- The one-pot conversion of fructose based carbohydrates can generate EMF yield around 55%.
- The catalyst was stable and could be reused.

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ABSTRACT

Catalytic conversion of carbohydrates into valuable chemical and liquid fuels has received considerable attention in recent years. In this study, sulfonic acid-functionalized ordered mesoporous carbon (OMC-SO₃H) was prepared and well characterized by physical techniques such as TEM, nitrogen physisorption measurements and XRD. The as-prepared OMC-SO₃H was then used for the acid-catalyzed conversion of fructose based carbohydrates into 5-hydroxymethylfurfan (HMF) or 5-ethoxymethylfurfural (EMF). Due to the high surface area and high acidity, the OMC-SO₃H catalyst showed a comparable catalytic performance as the homogeneous catalysts. The dehydration of fructose over the OMC-SO₃H catalyst produced a high HMF yield of 89.4% in DMSO at 120 °C within 30 min. The one-pot transformation of fructose carbohydrates were also smoothly performed, affording EMF yields of 55.7%, 53.6% and 26.8% from fructose, iuline and sucrose after 24 h at 140 °C, respectively. Furthermore, the OMC-SO₃H catalyst can be reused and no apparent loss of the activity was observed.

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1. Introduction

Currently, there is a growing attention on the search of renewable resources to provide chemicals and fuels for our society, due to the diminishing fossil reserves [1,2]. Biomass as the only material renewable resource has received great interest for the production of fuels and chemicals [3,4]. It was predicted that 18% of all manufactured chemicals will originate from biomass by 2020 via biorefinery [5]. Therefore, a considerable effort has been devoted to transform of biomass resources into value-added chemicals

and liquid fuels via various technologies [6–8]. Among them, catalytic routes seem to be very crucial, as various chemicals and fuels can be produced by careful design of different catalytic routes [9–11].

Carbohydrates represent the major component of biomass. The dehydration of C6 carbohydrates can generate one of the most important platform chemicals- 5-hydroxymethylfurfan (HMF) [12,13]. Through biorefinery, HMF can be transformed into a variety of chemicals, polymer precursor, and liquid fuels [14,15], which are mainly obtained from the non-renewable fossil fuels resources or can be used as alternatives to chemicals from fossil fuels. Due to the significance of HMF in the linkage of the gap between renewable resources to fossil resources, the catalytic transformation of carbohydrates into HMF has been extensively

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studied during the past decades [16,17]. The acid-catalyzed dehydration of fructose is the most efficient method, generally with high HMF yields. Among HMF derivatives, 5-ethoxymethylfurfural (EMF), which is product of the acid-catalyzed etherification of HMF, has recently been attracted great interest as a potential liquid fuel [18–20]. EMF has a high energy density of 30.3 MJ L^{-1} , which is very close to that of diesel (33.6 MJ L^{-1}), and 29% higher than that of ethanol. In addition, EMF also generates positive results in engine tests with a significant reduction of soot and SO_x emissions.

The transformation of fructose based carbohydrates into HMF or EMF has been performed by the use of homogeneous and heterogeneous catalysts. The one-pot conversion of fructose into EMF contains two consecutive reactions, which involves the acid-catalyzed dehydration of fructose into HMF, and the subsequent acid-catalyzed etherification of HMF with ethanol to produce EMF (Scheme 1). In early work, commercial H_2SO_4 was used for the conversion of fructose into EMF with a yield about 60% [21]. Later, some other homogeneous catalysts such as acidic-ionic liquids and Lewis acid were also used for the synthesis of EMF from fructose based carbohydrates [22,23]. Obviously, the use of homogeneous catalysts demonstrated several drawbacks such as the difficulty in the reuse of the catalyst and the release of toxic waste to the environments. The use of heterogeneous catalysts can overcome these above mentioned drawbacks. Various kinds of heterogeneous catalysts have been applied for the synthesis of EMF [24]. However, some of the heterogeneous catalytic system still demonstrated shortcomings. For example, the HPW/MCM-41 catalyst only produced EMF in a relative low yield of 42.9% after 24 h at 110°C [25]. Therefore, it is still required to develop new and efficient catalytic systems for the transformation of fructose based carbohydrates into EMF.

Carbon nanomaterials have been shown promising application in the development of sustainable catalysts for green chemistry. In order to facilitate the absorption of reactant molecules on the surface of the carbon catalysts, in this study, sulfonic acid-functionalized ordered mesoporous carbon (OMC) was prepared and used for the synthesis of HMF and EMF from fructose based carbohydrates.

2. Experiments

2.1. Materials

Resorcinol, formaldehyde and chlorosulfonic acid were purchased from Aladdin Chemicals Co. Ltd. (Beijing, China). Pluronic F127 (17.6 g) was purchased from Sigma-Aldrich Co. Ltd. Fructose was purchased from Sanland-Chem International Inc. (Xiamen, 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). All the chemicals were obtained commercially and used without any further purification.

2.2. Preparation of the catalyst

2.2.1. Preparation of the mesoporous carbon

Mesoporous carbon was prepared according to the known method with a slight modification [26]. Resorcinol (4.4 g) and

pluronic F127 (4.4 g) were firstly dissolved in ethanol (18 mL)/water (14 mL)/HCl (4.4 mL, 4.3 m). To this solution, formaldehyde (5.2 mL) was added, and then the mixture was stirred for 60 min. After that, the liquid phase was decanted, and the bottom gel polymer was casted on Mylar. The film was dried overnight at room temperature and then at 80°C for 24 h. The obtained polymer composite was carbonized under nitrogen atmosphere (500 mL min^{-1}) at 850°C for 120 min at a heating rate of 5°C min^{-1} . This sample was labeled as OMC.

2.2.2. Preparation of the acid catalyst

OMC (1.0 g) was dispersed in chlorosulfonic acid (25 mL), and the mixture was stirred at 100°C for 48 h under flowing N_2 . Then, the mixture was filtrated and washed with water until the filtrate was neutral. The catalyst was dried at 60°C in a vacuum oven overnight. The as-made sulfonic acid functionalized OMC catalyst was denoted as OMC- SO_3H .

2.3. Catalyst characterization

Transmission electron microscope (TEM) images were performed on an FEI Tecnai G^2 -20 instrument. The OMC- SO_3H catalyst was firstly dispersed in ethanol and dropped onto copper grids for observation. X-ray powder diffraction (XRD) patterns of the OMC- SO_3H catalyst was performed on a Bruker advanced D8 powder diffractometer (Cu $K\alpha$). The XRD pattern of the OMC- SO_3H catalyst was collected in the 2θ range of 10 – 80° with a scanning rate of $0.016^\circ/\text{s}$. Nitrogen physisorption measurements were conducted at 77 K on a quantachrome Autosorb-1-C-MS instrument.

2.4. Titration of the acidity

The amount of H^+ in the OMC- SO_3H was determined by acid-base titration. Briefly, OMC- SO_3H (0.5 g) was stirred in 20 mL of saturated NaCl solution for 24 h. During this step, the H^+ was completely liberated into the reaction solution by the exchange with Na^+ . The liberated H_3O^+ was then titrated by standard NaOH solution.

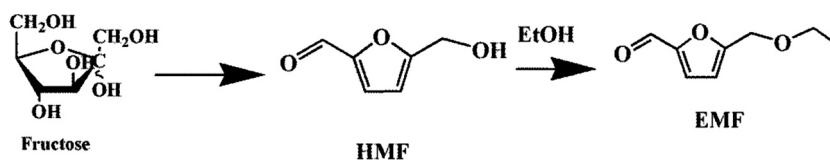
2.5. General procedure

2.5.1. Catalytic dehydration of fructose into HMF

Typically, fructose (90 mg, 0.5 mmol) was dissolved in Dimethyl sulphoxide (DMSO, 5 ml) and OMC- SO_3H catalyst (30 mg) was added. The reaction was carried out at 120°C for 30 min with a magnetic stirring rate of at 600 rpm (rpm). After reaction, a small aliquot was withdrawn from the reaction mixture, and diluted with deionized water to a certain concentration for HPLC detective range.

2.5.2. Synthesis of EMF from fructose based carbohydrates

Typically, fructose (0.5 mmol, 90 mg), OMC- SO_3H catalyst (100 mg) was added to ethanol (5 mL). Then the reaction was carried out at 140°C for 24 h. After reaction, the mixture was transferred to a 25 ml volumetric flask. Then, it was further diluted to a certain volume, and centrifugated. The liquid solution was analyzed by HPLC.



Scheme 1. Schematic illustration of the one-pot synthesis of EMF from fructose.

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