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Magnetic lignin-derived carbonaceous catalyst for the dehydration of fructose into 5-hydroxymethylfurfural in dimethylsulfoxide

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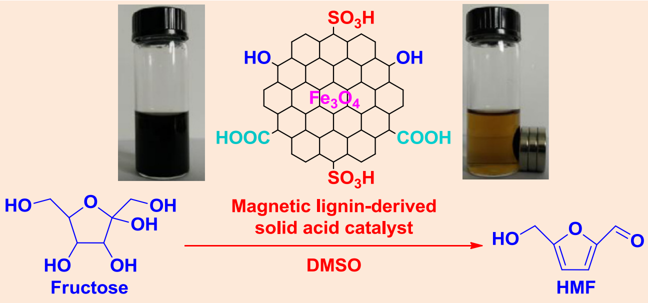
HIGHLIGHTS

- A magnetic lignin-derived catalyst (MLC-SO_3H) was prepared and characterized.
- MLC-SO_3H possessed a porous structure and a high surface area.
- MLC-SO_3H was effective for the dehydration of fructose into HMF in DMSO.
- MLC-SO_3H could be easily separated by using an external magnet.

GRAPHICAL ABSTRACT

A magnetic lignin-derived carbonaceous solid acid catalyst was very effective for the dehydration of fructose into HMF in the presence of DMSO.



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ABSTRACT

A magnetic carbonaceous catalyst was prepared by a simple and inexpensive impregnation–carbonization–sulfonation process using the enzymatic hydrolysis lignin residue as a precursor. The resulting catalyst possessed a porous structure with a high surface area and contained Fe_3O_4 components and —SO_3H, —COOH and phenolic —OH groups, and it showed a good catalytic activity for the dehydration of fructose into 5-hydroxymethylfurfural (HMF). By optimizing the reaction conditions, a high HMF yield of 81.1% with 100% fructose conversion was achieved in the presence of dimethylsulfoxide (DMSO) at 130 °C for 40 min. More importantly, the magnetic lignin-derived carbonaceous catalyst could be easily separated from the reaction mixture by using an external magnet, and when it was reused 5 successive runs, no obvious decrease in the yield of HMF was observed, indicating that the magnetic lignin-derived carbonaceous catalyst also exhibited an excellent catalytic stability.

1. Introduction

In recent years, increasing worldwide energy demands together with diminishing fossil resources and growing concerns about environmental pollution and global warming have led to an increasing research interest in the conversion of renewable biomass resources into various chemicals [1–5]. Among many possible chemicals, 5-hydroxymethylfurfural (HMF), which has been listed as the top

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10 bio-based chemicals by the U.S. Department of Energy, is considered to be one of the most promising platform compounds [6–9], because it can be used as a versatile precursor for the synthesis of a sequence of high-quality fuels l and solvents such as liquid alkane, 2,5-dimethylfuran (DMF), 5-ethoxymethylfurfural (EMF), 1,2,6-hexanetriol (HT) and 2,5-dihydroxymethyltetrahydrofuran (DHMTHF) [10–15] and high-value polymers and surfactants such as 2,5-dihydroxymethylfurfural (DHMF), 2,5-diformylfuran (DFF), 2,5-furandicarboxylic acid (FDCA), p-xylene and 5-dioctyloxymethyl-2-furanmethanol (DOMFM) [16–23]. At present, HMF can be synthesized through the dehydration of all types of biomass-derived C_6 carbohydrates such as fructose, glucose, sucrose, maltose, starch and cellulose. However, it should be pointed out that relative to other carbohydrates, the production of HMF from fructose is much easier, which is due to the fact that the furanoid structure of fructose is more reactive to dehydration [24]. Hence, fructose has always been selected as a preferred starting material for the production of HMF [25–28].

As reported in many literatures, water is the most ideal solvent for the dehydration of fructose into HMF in theory [29], this is because that water has great advantages in the economical viability, ecological superiority and technological convenience [24]. Unfortunately, the dehydration of fructose is non-selective in pure water, leading to a low yield of HMF, which is caused by the formation of an abundance of byproducts such as levulinic acid (LA), formic acid (FA) and humins [30–32]. To improve the yield of HMF and suppress the formation of byproducts, ionic liquids, a new type of solvents with high selectivities in the dehydration of fructose, have attracted much attention because of their unique physicochemical properties such as negligible vapor pressure, low melting point, high thermostability, intrinsic nonflammability, remarkable solubilizing ability and infinite structural variation [33]. However, ionic liquids are not desirable for the large-scale applications, the main reason is that their costs are too high in the present techniques [34–36]. Encouragingly, dimethylsulfoxide (DMSO), which is well known for dissolving hexoses, stabilizing HMF and reducing side-reactions [3,22,24,32], has been extensively investigated by many researchers and used as a good solvent for the dehydration of fructose into HMF.

In addition to search for an appropriate solvent, the design of a green and efficient acid catalyst is another key point for the dehydration of fructose into HMF. Up to now, many types of acid catalysts including homogeneous acid catalysts such as mineral acids [37], organic acids [38] and metal chlorides [39] and solid acid catalysts such as H-zeolites [40], metal oxides [41], ion-exchange resins [42], supported heteropoly acids [43], functionalized inorganic–organic nanoparticles [44] and transition metal phosphates [45] have been explored and applied to this reaction. Although homogeneous acid catalysts are inexpensive and active for the dehydration of fructose into HMF, the large-scale applications are difficult due to their strong corrosion to reactors and high toxicity to environments as well as their recycling problems. From an environmental and economic point of view, solid acid catalysts are more advisable for the dehydration into HMF, because they are less corrosive and easier to separate and recycle. Compared to the above-mentioned conventional solid acid catalysts, the more cheaper carbon-based solid acid catalysts, which are generally prepared by the incomplete carbonization of glucose or cellulose and the subsequent sulfonation of the resulting amorphous carbon, have been identified as a novel type of solid acid catalysts in recent years and also widely employed for the dehydration of fructose into HMF [46–48]. However, carbon-based solid acid catalysts possess a common drawback related to the lower specific surface areas, which can limit their catalytic activities for the dehydration of fructose into HMF. Moreover, carbon-based solid acid catalysts cannot be readily separated with the formed solid residues such as humins, which can affect their recyclabilities. Therefore, the development of an easy-to-separate carbon-based solid acid catalyst with a high specific surface area is necessary and important for the dehydration of fructose into HMF.

Inspired by the present research situations and existing issues, a magnetic carbon-based solid acid catalyst was synthesized by using the enzymatic hydrolysis lignin residue (EHL) as a precursor via a simple and inexpensive process involving impregnation, carbonization and sulfonation. Subsequently, the prepared magnetic lignin-derived carbonaceous solid acid catalyst was systematically characterized by X-ray diffraction (XRD) spectroscopy, X-ray photoelectron (XPS) spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, Raman spectroscopy, scanning electron microscopy (SEM), thermogravimetric analysis (TGA), nitrogen adsorption–desorption, elemental analysis and acid–base titration and then used for the dehydration of fructose into HMF in the presence of DMSO. In order to obtain a higher yield of HMF, various reaction parameters such as reaction temperature, reaction time, catalyst loading and fructose concentration were optimized in detail. Furthermore, the recyclability of catalyst was also investigated to evaluate its catalytic stability.

2. Materials and methods

2.1. Materials

HMF (99%) and Amberlyst-15 were supplied by Shanghai Energy Chemical Co. Ltd. (Shanghai, China). Hβ-zeolite was purchased from Novel Chemical Technology Co. Ltd. (Shanghai, China). 1-Butyl-3-methylimidazolium chloride ([BMIM]Cl) was supplied by Shanghai ChengJie Chemical Co. Ltd. (Shanghai, China). DMSO, fructose, dimethylacetamide (DMA), methyl isobutyl ketone (MIBK), concentrated sulfuric acid (H_2SO_4), sodium hydroxide (NaOH), barium chloride ($BaCl_2$) and ferric chloride ($FeCl_3$) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) and used without further purification. EHL, which was obtained from the enzymatic hydrolysis of corn stover in the production of lignocellulosic ethanol, was supplied by Anhui Fengyuan Group Co. Ltd. (Anhui, China).

2.2. Catalyst preparation

EHL was initially washed with deionized water and ethanol to remove impurities, respectively, and dried in a vacuum oven at 65 °C for 12 h. The dried EHL was then grinded to 120 mesh and used as a precursor for the preparation of catalyst. Subsequently, 10 g grinded EHL was added into 1000 mL $FeCl_3$ solution with a concentration of 10 mmol L^{-1}, and the mixture was stirred at 300 rpm for 5 h. Then, the water in the mixture was evaporated, and the remaining mixture was dried in a vacuum oven at 65 °C for 12 h. After grinding again to 120 mesh, the impregnated EHL with a Fe content of approximately 1 mmol g^{-1} was obtained.

Whereafter, the Fe-impregnated EHL was carbonized at 400 °C for 1 h under nitrogen atmosphere to produce the magnetic lignin-derived amorphous carbon (MLC). And then, the resulting MLC was mixed with concentrated H_2SO_4 (the ratio of solid and liquid = 1:10), and the mixture was heated at 150 °C for 10 h under nitrogen atmosphere to introduce $-SO_3H$ groups. Soon afterwards, the mixture was cooled to room temperature and diluted with 1000 mL deionized water, which was followed by filtrating and washing with hot deionized water (>80 °C) until the sulfate ions were no longer detected in the washed water. Finally, the resulting catalyst, which was denoted as MLC-SO_3H, was dried in a vacuum oven at 65 °C for 12 h. For comparison, another carbon-based catalyst (LC-SO_3H) was also synthesized in the same procedure using EHL without Fe-impregnating as a precursor.