



Catalytic conversion of xylose and corn stalk into furfural over carbon solid acid catalyst in γ -valerolactone



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HIGHLIGHTS

- The catalyst SC-CCA was prepared utilizing sucrose which is a biomass material.
- An efficient and eco-friendly method for furfural production was proposed.
- Furfural yield of 78.5% from xylose was achieved.
- 60.6% furfural yield were obtained from raw corn stalk.
- The catalyst can be reused at least for 5 runs.

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ABSTRACT

A novel carbon solid acid catalyst was synthesized by the sulfonation of carbonaceous material which was prepared by carbonization of sucrose using 4-BDS as a sulfonating agent. TEM, N₂ adsorption–desorption, elemental analysis, XPS and FT-IR were used to characterize the catalyst. Then, the catalyst was applied for the conversion of xylose and corn stalk into furfural in GVL. The influence of the reaction time, temperature and dosage of catalyst on xylose dehydration were also investigated. The Brønsted acid catalyst exhibited high activity in the dehydration of xylose, with a high furfural yield of 78.5% at 170 °C in 30 min. What's more, a 60.6% furfural yield from corn stalk was achieved in 100 min at 200 °C. The recyclability of the sulfonated carbon catalyst was perfect, and it could be reused for 5 times without the loss of furfural yields.

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1. Introduction

Nowadays, with the rapid development of economy, the human demand for energy is growing fast. Most fuel and many other necessary chemicals are derived from petroleum. But the continued growth of human dependence on fossil sources and limited petroleum reserves have led to a series of compelling global problems, including climate change such as the “greenhouse effect” and war over resources in many areas (Bernal et al., 2014). Therefore, the subject of finding alternative ways to fulfill the energy needs has become the focus of the whole society. Lignocellulosic biomass as a abundant and renewable source is considered to be very

promising in producing high value-added chemicals (Zhang et al., 2014) and biofuels (Lange et al., 2012). Furfural can be derived from pentosan-rich lignocellulosic biomass which is a key feedstock that can be transformed into important non-petroleum-chemicals and bio-fuels (Agirrezabal-Telleria et al., 2014a). Furfural is considered one of the most promising materials to produce sustainable fuels and chemicals in the 21st century (Bozell and Petersen, 2010).

Furfural can be used to produce many useful chemicals, such as furfuryl alcohol, 2-methylfuran, tetrahydrofuran, cyclopentanone (Yan et al., 2014), and γ -valerolactone (GVL) (Bui et al., 2013). Furfural and its derivatives have a variety of applications in the oil-refining, plastic, pharmaceutical and agrochemical industries (Li et al., 2014).

In the past decades, the dehydration of xylose, xylan, corn stalk, bagasse and some other feedstocks to produce furfural has been

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extensively studied. Both homogeneous and heterogeneous catalysts have been investigated for furfural production. Sulfuric acid was used as catalyst for furfural manufacture in 1921 (Yan et al., 2014). Even now, the commercial production of furfural from lignocellulosic biomass is catalyzed by mineral acid (H_2SO_4 or HCl) (Bernal et al., 2014). Yemis and Mazza (2011) compared the yields of furfural using a range of inorganic and organic acids as catalysts (hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, acetic acid, formic acid) in a microwave-assisted reaction system. Hydrochloric acid was found to give the highest furfural yield from xylose at 37.5%. Other efficient homogeneous catalysts containing Lewis acid such as FeCl_3 (Zhang et al., 2014; Mao et al., 2012) and AlCl_3 (Zhang et al., 2013) gave a furfural yield higher than 60%. Nevertheless, the major disadvantages of using homogeneous catalysts are: (1) homogeneous catalysts like mineral acids are extremely corrosive to the equipment, (2) the post-reaction separation between homogeneous catalysts and substrate is difficult, and (3), homogeneous catalysts cannot be reused (Chen and Fang, 2011; Agirrezabal-Telleria et al., 2013).

Recently, researchers have paid more attention to the development of efficient heterogeneous catalysts (Agirrezabal-Telleria et al., 2014b). Due to their easy separation after the reaction and reutilization, heterogeneous catalysts are the most promising for commercial production (Agirrezabal-Telleria et al., 2014a). Zeolite and related functionalized zeolite catalysts such as MCM-41 (Zhang et al., 2012), MCM-41-supported niobium-oxide (García-Sancho et al., 2013), SBA-15- SO_3H (Shi et al., 2011) and silica-poly(styrenesulphonic acid) (Sádaba et al., 2014) with micromesoporous are highly effective in the conversion of xylose to furfural. Especially, the interaction between H_3PO_4 and Mordenite-13 shows a molar yield of furfural with 98% (Lessard et al., 2010). There have been reports of catalytic activity research of different cation exchange resin catalysts including Amberlyst-15 (Ordomsky et al., 2013), Amberlyst-70 (Gürbüz et al., 2013) and nafion-117 (Lam et al., 2011). Other solid acids, such as functionalized partially hydroxylated MgF_2 (Agirrezabal-Telleria et al., 2013), $\text{SO}_4^{2-}/\text{TiO}_2\text{-ZrO}_2/\text{La}^{3+}$ (Li et al., 2014) and mesoporous Nb_2O_5 (García-Sancho et al., 2014) have also been studied for dehydration reaction. Functionalized partially hydroxylated MgF_2 has active sites for both Brønsted and Lewis acids, and it has been proven that a high furfural yield can be achieved. In addition to the above heterogeneous catalysts, carbon-based solid acid catalysts also have high catalytic activity. So far, more and more studies have been focused on the carbon-based solid acids. Carbon was chosen as a support because of its high surface activity and thermal stability under the high temperature of the dehydration reaction (Lam et al., 2012). The two-step synthesis of carbon solid acids consists of the preparation of carbonaceous materials followed by sulfonation of carbonaceous materials. Graphene oxide (Ji et al., 2011), activated carbon (Geng et al., 2011) and the biomass-derived carbon produced by carbonization of raw materials such as glucose (Guo et al., 2012), sucrose (Geng et al., 2011), fructose (Guo et al., 2012), glucose-starch (Chen and Fang, 2011), cellulose (Guo et al., 2012; Kang et al., 2012) and lignin (Kang et al., 2012) can all be sulfonated by concentrated sulfuric acid (>98%) or 4-benzenediazoniumsulfonate (4-BDS). Suganuma et al. (2008) reported that amorphous carbon bearing SO_3H , COOH , and OH groups was applied to hydrolyze cellulose. The amorphous carbon was prepared by the partial carbonization of cellulose and then a sulfonation reaction was carried out by fuming sulfuric acid (15% SO_3). Although heterogeneous catalysts exhibit high catalytic properties, the deposition of by-product may cause the catalyst deactivation due to fouling and/or poisoning; in addition, the hydrothermal stability of some solid catalysts is very poor (Sádaba et al., 2014).

With the aim of improving the yield of furfural in a greener way, a number of solvent systems have been developed. Water is the

most eco-friendly and inexpensive solvent, so it has been used to manufacture furfural industrially. But water is a highly polar protic solvent, and consequently the yield of furfural is very low (Mellmer et al., 2014). Thus, alternative monophasic systems, dimethyl sulfoxide (DMSO) (Lam et al., 2011), tetrahydrofuran (THF) (Mellmer et al., 2014), 1-butanol (Zhang et al., 2012), ionic liquids (Zhang et al., 2013) have been investigated for the furfural preparation. In addition, biomass-derived GVL as a monophasic solvent for acid-catalyzed reactions reveals significant improvement compared to the conversion of xylose in water (Mellmer et al., 2014). For xylose dehydration, GVL can increase the reaction rates without the loss of formed furfural. Most importantly, GVL is a green and nontoxic solvent which possesses vast potential for application in the production of furfural. After reactions, furfural in GVL can be easily separated by distillation.

Interestingly, biphasic systems such as water/toluene (Lessard et al., 2010; Agirrezabal-Telleria et al., 2013; Sádaba et al., 2014; García-Sancho et al., 2014), water/isobutylmethylketone (MIBK) (Weingarten et al., 2010) which consist of water and an organic solvent are more efficient. Furfural produced in the biphasic system is extracted into organic phase so that it can prevent loss from undesired side reactions between furfural and an intermediate or other compounds.

It has been reported that disordered mesoporous carbon with high specific surface area and large pores is prepared from carbon-coated alumina (CCA), which is synthesized through carbon precursor adsorption-pyrolysis. Then combined benzenesulfonic acid groups with the carbon material by 4-BDS to generate solid acid catalyst (Geng et al., 2011). Using 4-BDS as a sulfonating agent instead sulfuric acid simplifies the process of yielding catalyst. This kind of catalyst is readily dispersed in GVL. The catalyst may provide high catalytic efficiency for the production of furfural from xylose and corn stalk. In this work, we studied the preparation of furfural from xylose and corn stalk through dehydration catalyzed by the carbon solid acid in GVL. The catalyst was synthesized and characterized by a series of techniques to clarify the structure of the catalyst that gave high yield of furfural. The influence of the reaction time, temperature and the dosage of catalyst on the conversion of xylose and the furfural yield were studied. The stability and reusability of the carbon catalyst were also investigated.

2. Methods

2.1. Materials

D-(+)-xylose ($\geq 99\%$), furfural (99%), hydrochloric acid (HCl , 36–38%), sodium nitrite (NaNO_2 , AR), N,N-dimethylformamide (DMF, AR) and acetone were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Sucrose (AR), sulfanilic acid (AR), γ -alumina ($\gamma\text{-Al}_2\text{O}_3$, 99.99%) and hydrofluoric acid (HF, 40%) were obtained from Aladdin Industrial Inc. (Shanghai, China). γ -GVL (95%) was purchased from LangFang Hawk Technology and Development Co., Ltd. Corn stalk was collected from Bozhou, China. The raw material was ground until the whole sample passed through a 40-mesh screen, and then washed with deionized water to remove dust on the material. After that, the corn stalk was dried in an oven at 80°C for 48 h.

2.2. Catalyst preparation

The carbonaceous material and 4-BDS were synthesized according to the methods described in literature (Geng et al., 2011; Ji et al., 2011) with slight modifications. 9 g of $\gamma\text{-Al}_2\text{O}_3$ was impregnated with a clear solution of sucrose (9 g). After ultra-sonicated for 30 min, the mixture was dried at 80°C in an oven. The dried white solid was ground to fine powder in a mortar. The

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