Fuel Processing Technology 169 (2018) 244–247

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Research article

Hydrolysis of cellulose with one-pot synthesized sulfonated carbonaceous solid acid

Feng Shen, Tianmeng Guo, Chenxi Bai, Mo Qiu, Xinhua Qi*

Agro-Environmental Protection Institute, Chinese Academy of Agricultural Sciences, No. 31, Fukang Road, Nankai District, Tianjin 300191, China

ARTICLE INFO

Keywords:
Cellulose
Reducing sugars
Sulfuric acid-free preparation
Ionic liquid
Solid acid

ABSTRACT

Cellulose could be effectively hydrolyzed into reducing sugars with a novel sulfonated carbonaceous solid acid. The catalyst bearing both cellulose catalytic sites (–SO_3H) and binding sites (–Cl) was synthesized by one-pot carbonization of sucralose with *p*-toluenesulfonic acid, bypassing the use of concentrated sulphuric acid and without any post-modification. Influences of reaction time and temperature, water content in ionic liquid, dosage of catalyst and substrate on the yield of total reducing sugars (TRS) from cellulose were investigated. A maximum TRS yield of 67.6% was obtained in the 1-butyl-3-methyl imidazolium chloride at 130 °C in 60 min, which was much higher than that hydrolyzed by the –Cl free solid acid (36.1%). The excellent catalytic performance of the prepared solid acid can be attributed to the synergic effect of –SO_3H and –Cl groups. This work provided a green method to synthesize sulfonated carbonaceous solid acid for efficient conversion of biomass into biofuels.

1. Introduction

The transformation of renewable resources such as lignocellulose into fuels and chemicals has aroused increasing attention since it can be an alternative to the exhausted fossil fuels [1–3]. Cellulose, the main component of lignocellulose, is the most abundant carbohydrate polymer in nature and it can be converted into various kinds of high value-added chemicals and fuels such as 5-hydroxymethylfurfural, levulinic acid and ethylene glycol [4–7].

Generally, the conversion of cellulose into fuels and chemicals contains two reaction steps: the hydrolysis of cellulose and subsequent transformation of the formed sugars into chemicals and fuels. Hydrolysis of cellulose into reducing sugars is thus the starting point of cellulose utilization processes. However, it is the most difficult step due to the recalcitrant nature of cellulose. Up to now, several methods including biological, physical and chemical process have been used for the hydrolysis of cellulose. Cellulase can be used to hydrolyze cellulose into glucose with high selectivity, but the high cost of cellulase and long reaction time limit its industry application. The acid catalysts such as HCl, H_2SO_4 and heteropoly acid are effective to transform cellulose into reducing sugars [8–10]. However, these liquid acids suffer from disadvantages such as corrosion of equipment, waste acid release and catalysts non-recyclability [11]. Recently, much attention has focused on solid acid catalysts since they have advantages of environmental friendly, high stability and easy recyclability. Solid catalysts used for cellulose hydrolysis contains resins [12], silica/carbon nanocomposites [13], H-zeolite [14] and sulfonated carbonaceous acid [15,16]. Among them, carbonaceous acids, which are typically synthesized by the carbonization of biomass followed by –SO_3H modification with concentrated sulfuric acid or oleum [17,18], have gained more and more attentions since they can be synthesized from natural biomass. Unfortunately, the involvement of highly corrosive sulfuric acid or oleum is hazardous and large amount of the extra acid waste was released into environment. Moreover, the total reducing sugar yields from cellulose hydrolyzed by sulfonated carbonaceous solid acids were generally relatively low, attributing to the mass transfer limitation between the insoluble solid acid catalysts and cellulose. Therefore, more efforts have to be made to prepare novel sulfonated carbonaceous solid acid catalysts with green method other than concentrated sulfuric acid impregnation and have excellent catalytic performance in cellulose hydrolysis.

In this work, a novel sulfonated carbonaceous solid acid was facilely synthesized with one-step method in which sucralose and *p*-toluenesulfonic acid (TsOH) were used as the carbon precursor and in-situ sulfonation agent, respectively, avoiding the post-modification with concentrated sulfuric acid. In addition, sucralose as the carbon precursor can provide –Cl groups in the prepared solid acid. Previous studies demonstrated that –Cl can act as cellulose-binding domain thus improving the contact of cellulose molecules with solid acid catalyst [18–21]. The prepared carbonaceous solid acid bearing –Cl and –SO_3H groups exhibited higher activity than that bearing only –SO_3H groups,

---

* Corresponding author.
E-mail address: qixinhua@nankai.edu.cn (X. Qi).

http://dx.doi.org/10.1016/j.fuproc.2017.10.015
Received 21 August 2017; Received in revised form 20 October 2017; Accepted 21 October 2017

for the hydrolysis of cellulose in ionic liquid.

2. Method

2.1. Materials

Sucralose and *p*-toluenesulfonic acid were purchased from Beijing J & K Co., Ltd. (Beijing, China). 1-Butyl-3-methylimidazolium chloride ([BMIM][Cl]) (99%) was purchased from Henan Lihua Pharmaceutical Co., Ltd. (Xinxiang, China). Microcrystalline cellulose was provided by the Boya Company (Tianjin, China).

2.2. Synthesis of the sulfonated carbonaceous solid acid catalyst

Sucralose (4 g) and *p*-toluenesulfonic acid (TsOH) (4 g) were mixed with a mortar and were transferred into a 50 ml Teflon-lined autoclave. The autoclave was placed in a muffle furnace and the carbonization was conducted at 180 °C for 24 h. The obtained material was washed several times with ultra-pure water and ethanol, respectively. After that, the material was dried in an oven for 12 h at 80 °C. The as-prepared catalyst was denoted as SA-TsOH. A controlling catalyst was prepared in the same way but sucrose was used as the carbon precursor instead of sucralose, and the obtained solid sample was denoted as SO-TsOH.

2.3. Catalyst characterization

The Cl in the catalysts was detected by ICP-9000 (Thermo Jarrell-Ash Corp., USA). XRD was performed with a D8 Advance LynxEye Diffractometer. The FT-IR spectra of the catalysts were recorded with a 4 cm^{-1} resolution on Nicolet NEXUS-470 FTIR equipment (Madison, USA).

2.4. Hydrolysis of cellulose with the prepared solid acid

Typically, 0.05 g of cellulose was dissolved in1 g of [BMIM][Cl]. Then, 0.05 g of solid acid and 0.075 g of distilled water were added. The mixture was subsequently heated to a given temperature in an oil bath in a closed reactor for a certain reaction time. At the end of the reaction, the reactor was cooled with cold water and the mixture was diluted with 9 ml distilled water. Samples were then filtered and subjected to total reducing sugar (TRS) analysis with the reported 3, 5-dinitrosalicylic acid method [22]. The yield of TRS was calculated using Eq. (1):

$$\text{TRS yield (mol\%)} = \frac{\text{Moles of the produced reducing sugars in products}}{\text{Theoretical moles of glucose unit in the loaded sample}} \times 100\% \tag{1}$$

For the recycling experiments, after the first reaction for 60 min at 130 °C, the solid residue was recovered by filtration and then washed with hot water for several times. After drying in an oven for 12 h at 80 °C, the catalyst was used for the next run at identical reaction conditions (0.05 g cellulose, 1 g [BMIM][Cl], 0.05 g SA-TsOH, 130 °C, 60 min and 0.075 g H_2O). This recycling process proceeded repeatedly for eight times.

3. Results and discussion

3.1. Characterization of the prepared catalyst

XRD patterns of the prepared samples were given in Fig. S1. For both SA-TsOH and SO-TsOH, there is a strong diffraction peak at 2θ = 10–30 °C and a weak but broad peak at 35–50 °C. These XRD patterns are typical of amorphous carbonaceous materials [23]. Fig. S2 shows the FTIR spectra of the SA-TsOH and SO-TsOH. The band at 3400 cm^{-1} and 1600 cm^{-1} are attributed to –OH and –C–C stretching vibrations, respectively. The vibration bands at 1060 cm^{-1} was assigned to the $-SO_3$ group [17]. Both of SA-TsOH and SO-TsOH had these groups. Vibration band at 748 cm^{-1} corresponding to –Cl group, which could only be observed in the FTIR spectra of the SA-TsOH sample. ICP-AES measurements revealed that the Cl content of SA-TsOH and SO-TsOH were 1.03% (w/w) and 0% (w/w), respectively (Table S1).

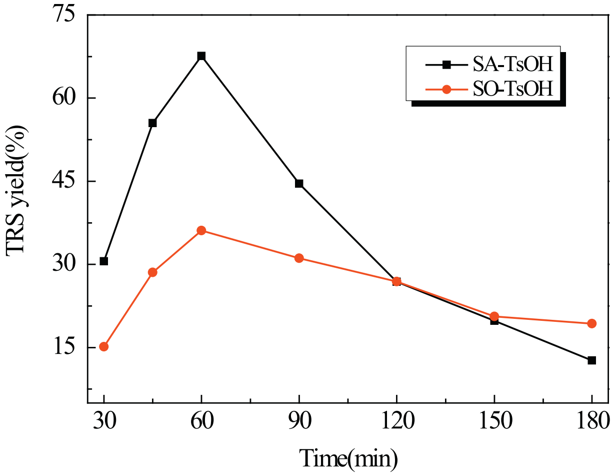

Fig. 1. TRS yield from cellulose catalyzed by SA-TsOH and SO-TsOH in [BMIM][Cl] (Reaction conditions: 130 °C, 0.05 g cellulose, 0.05 g catalyst, 0.075 g H_2O, 1 g [BMIM][Cl]).

3.2. Hydrolysis of cellulose with SA-TsOH and SO-TsOH

The prepared catalysts were applied for the direct transformation of cellulose into reducing sugars in ionic liquid of [BMIM][Cl] at 130 °C, and the results are shown in Fig. 1. When SO-TsOH was used to hydrolyze cellulose, a maximum TRS yield of 36.1% was achieved in 60 min, which can be attributed to the $-SO_3H$ groups in the SO-TsOH catalyst. When SA-TsOH was employed, the maximum TRS yield was as high as 67.6% in 60 min, which was much higher than that with SO-TsOH as catalyst. As shown in Table S1, SA-TsOH and SO-TsOH have almost the same content of S (10.15% and 8.98%, respectively) but different content of Cl (1.05% and 0%, respectively). Therefore, the higher catalytic efficiency of SA-TsOH for cellulose hydrolysis should be probably attributed to the presence of –Cl group, which could act as the cellulose binding domain to improve the binding ability of solid acids to cellulose molecules by hydrogen-bond interactions due to its strong electronegativity [19,24]. A possible mechanism of cellulose hydrolysis by the prepared SA-TsOH was discussed in the as shown in Fig. S3. The maximum TRS yields obtained from cellulose catalyzed by the SA-TsOH herein was compared with the other solid acid catalysts (Table S2), indicating that the SA-TsOH catalyst obtained in this study showed better catalytic performance than most of the other solid acid catalysts such as HY-Zeolite, Nafion® NR50, and Fe_3O_4@C-SO_3H.

3.3. Influence of reaction time and temperature on the TRS yield

The effect of reaction time and temperature on the yield of TRS from cellulose catalyzed by the as-prepared SA-TsOH was investigated. As shown in Fig. 2, for all reaction temperatures, the TRS yield increased at the initial reaction times, but then remarkably decreased after reaching a maximum yield. This is because the TRS yield is determined by the equilibrium between cellulose hydrolysis and the reducing sugars decomposition [22]. At the beginning of the hydrolysis reaction, the cellulose hydrolysis rate was higher than the decomposition rate. Thus, the yield of TRS gradually increased. When the hydrolysis rate was equal to