Bioresource Technology 220 (2016) 457–463

Contents lists available at ScienceDirect

Bioresource Technology

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

The enhancement of the hydrolysis of bamboo biomass in ionic liquid with chitosan-based solid acid catalysts immobilized with metal ions

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HIGHLIGHTS

- SCCR immobilized with Cu^{2+}, Fe^{3+} and Zn^{2+} were firstly utilized in biomass hydrolysis.
- Fe^{3+}-SCCR solid acid catalyst can achieve a high TRS yield of 73.4%.
- These novel solid acid catalysts might be valuable for biomass utilization.

ARTICLE INFO

Article history:
Received 17 June 2016
Received in revised form 13 August 2016
Accepted 16 August 2016
Available online 18 August 2016

Keywords:
Chitosan
Solid acid catalyst
Ionic liquids
Metal ions
Biomass hydrolysis

ABSTRACT

Three kinds of sulfonated cross-linked chitosan (SCCR) immobilized with metal ions of Cu^{2+}, Fe^{3+} and Zn^{2+} individually were synthesized and firstly used as solid acid catalysts in the hydrolysis of bamboo biomass. FTIR spectra showed that metal ions had been introduced into SCCR and the N-metal ions coordinate bound was formed. The particle sizes of these catalysts were about 500–1000 μm with a pore size of 50–160 μm. All of the three kinds of catalysts performed well for bamboo hydrolysis with 1-butyl-3-methyl-imidazolium chloride used as solvent. The most effective one was sulfonated cross-linked chitosan immobilized with Fe^{3+} (Fe^{3+}-SCCR). TRS yields were up to 73.42% for hydrolysis of bamboo powder in $[C_4mim]Cl$ with Fe^{3+}-SCCR at 120 °C and 20 RPM after 24 h. These novel chitosan-based metal ions immobilized solid acid catalysts with ionic liquids as the solvent might be promising to facilitate cost-efficient conversion of biomass into biofuels and bioproducts.

1. Introduction

Due to the rapidly growing demand for fuels and environmental concerns stemming from the combustion of fossil fuels, it is important to utilize clean and renewable energy sources to produce fuels and chemicals. Lignocellulosic biomass has shown promise as an efficient renewable clean energy resource for biofuels and chemicals production (Demirbas, 2001). The crucial step in the production of biofuels or chemicals from biomass is the hydrolysis of cellulose to fermentable sugars (Jäger and Büchs, 2012; Ragauskas et al., 2006). However, the sugar molecules in lignocellulose are efficiently protected against chemical processing by β-glycosidic linkages (Himmel et al., 2007). Studies by Rogers et al. showed that cellulose and wood could dissolve in 1-butyl-3-methylimidazolium chloride ionic liquids (ILs), which made the cellulose chains accessible to chemical transformation (Swatloski et al., 2002; Wang et al., 2012). From then on, dissolution of lignocellulosic substrate in various kinds of ILs as an effective pretreatment method has attracted much more attention in the worldwide (da Costa Lopes et al., 2013; Weerachanchai and Lee, 2013; Sun et al., 2009).

Mineral acids as catalysts for the hydrolysis of lignocellulose were firstly studied by Wyman (1994). Recently, it is reported that mineral acids could also work well in ILs (Li and Zhao, 2007; Rinaldi et al., 2008; Sievers et al., 2009; Vanoye et al., 2009). Li and Zhao (2007) reported that a yield of 64% TRS was obtained after 42 min with an acid/cellulose mass ratio was 0.46. A soluble cellulose feedstock yield of 62% was achieved by Sievers et al. after

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http://dx.doi.org/10.1016/j.biortech.2016.08.064

2 h in the presence of 0.4 wt% trifluoroacetic acid, while loblolly pine wood was used as the feedstock (Sievers et al., 2009). The kinetics of the acid catalyzed hydrolysis of cellobiose in the ionic liquid was studied as a model for general lignocellulosic biomass hydrolysis in ionic liquid systems (Vanoye et al., 2009). The results showed the ratio of the reaction rate constant was $k_1/k_2 = 2.4$ for cellulose hydrolysis, so the anticipated yield in glucose was 50% (Vanoye et al., 2009). However, mineral acids can hardly be separated from the hydrolysate and reused. The corrosive characteristics of acids also add burden to the equipment maintenance. The use of solid acids holds on the advantages of using acid hydrolysis, but overcomes the current drawbacks of mineral acids (Guo et al., 2012; Shimizu and Satsuma, 2011; Zhang and Zhao, 2009; Wiredu and Amarasekara, 2014). Guo et al. (2012) found that compared with liquid acid catalysts, solid acid catalysts have distinct advantages in recycling, separation, and environmental friendliness. Solid acid catalysts are easily separated from the products mixture for reuse after reaction (Guo et al., 2012). Shimizu and Satsuma (2011) reported that mobile protonic acid could be formed from supported metal catalysts under pressurized hydrogen atmosphere, and the strong adsorption of cellulose by phenolic OH groups on the sulfonated carbon material caused the enhancement of the contact between a solid acid catalyst and solid cellulose. In another report, a silica-immobilized Brönsted acidic ionic liquid catalyst was synthesized and used for cellulose hydrolysis (Wiredu and Amarasekara, 2014). A silica immobilized imidazolium-type acidic ionic liquid catalyst was shown to be a better catalyst than n-propylsulfonic acid silica ($PrSO_3H\text{-}SiO_2$) and sulfonic acid silica ($SO_3H\text{-}SiO_2$) for the hydrolysis of untreated Sigmacell Cellulose (DP $\sim$ 450) in water (Wiredu and Amarasekara, 2014). New catalyst produced the highest TRS yield of 48.1% after 3 h at 190 °C, whereas cellulose samples heated with $PrSO_3H\text{-}SiO_2$ and $SO_3H\text{-}SiO_2$ catalysts produced only 19.9% and 13.2% TRS yields (Wiredu and Amarasekara, 2014). Hydrolysis of cellulose in ionic liquids catalyzed by a magnetically-recoverable solid acid catalyst was also investigated (Xiong et al., 2014). A core–shell $Fe_3O_4@SiO_2\text{-}SO_3H$ acid catalyst, which was prepared by the immobilization of sulfonic acid groups on the surface of silica-encapsulated Fe_3O_4 nanoparticles showed a good activity with RS yield of 73.2% (Xiong et al., 2014).

The efficient conversion of cellulose into furans catalyzed by metal ions in ionic liquids was also studied (Tao et al., 2012). Tao et al. (2012) reported that a co-catalysis performance of Cr^{3+}, Mn^{2+}, Fe^{3+}, Fe^{2+}, Co^{2+} were much better than other metal ions, microcrystalline cellulose conversion increased by 10–19%, and the selectivities of products were also improved obviously. Previous researchers used different types of transition metal salt catalyst, such as $FeCl_3$, $CuCl_2$, $AlCl_3$, during acid hydrolysis of cellulose (Kamireddy et al., 2013).

Chitosan, as a cheap and environmentally friendly natural polymer, can be modified as solid acid with the introduction of the acidic sites of SO_3H groups. The modified chitosan solid acids have shown efficient effects on various organic reactions (Kayser et al., 2014; Singh et al., 2013). Furthermore, chitosan is considered as a promising carrier for the immobilization of metal ions (Guibal et al., 2006). In our previous study, the effects of six metal ions: Na^+, K^+, Mg^{2+}, Ca^{2+}, Cu^{2+} and Fe^{3+} on hydrolysis of bamboo biomass by dilute hydrochloride acid in ionic liquid n-butylmethylimidazolium chloride was investigated (Wang et al., 2014). A total reducing sugar yield of 67.1%, using $CuCl_2$ as the co-catalyst, was achieved after 4 h at 100 °C. However, till now, no reports focused on the application of metal ions immobilized acidic chitosan in lignocellulose hydrolysis with IL as a green solvent, to our knowledge, while solid acid and metal ions both promote the hydrolysis (Wiredu and Amarasekara, 2014; Xiong et al., 2014; Tao et al., 2012; Wang et al., 2014).

In this study, sulfonated cross-linked chitosan immobilized with metal ions used as powerful catalysts for the hydrolysis of cellulose in ionic liquid was explored. Lignocellulosic materials, such as bamboo could be efficiently hydrolyzed using this methodology. Furthermore, the modified chitosan solid acid could be easily separated from the hydrolysate. This study provides a cost-efficient way for lignocellulose processing, which allows the large-scale use of cellulose depolymerization as the first step in biorefineries.

2. Materials and methods

2.1. Materials

The bamboo was obtained freely from a bamboo grove in Chongqing, China and milled to 80 mesh sieve. The main chemical composition of bamboo was determined using a two-step acid hydrolysis method developed by the National Renewable Energy Laboratory (NRTL) (Sluiter et al., 2011) with weight percent of the dry matter of 20.3% xylan, 22.3% lignin, 40.1% glucan (Wang et al., 2014).

ILs used in the system, namely 1-butyl-3-methyl-imidazolium chloride ($[C_4mim]Cl$), was prepared according to the method reported by Webb et al. (2003). The chitosan, with stated purities higher than 95% mass fraction, was purchased from Yuhuan Biochemical Co. Ltd. (Zhejiang, China).

2.2. Preparation of modified chitosan-based solid acid catalyst

Crosslinked chitosan resin (CCR) was synthesized following procedures as reported in the literatures (Xiao and Zhou, 2008). In the procedure of metal ions immobilization, 2 g dried CCR were added to 100 mL 1 mol/L solution of metal chloride. The reaction mixture was continuously stirred for 24 h at 25 °C and 200 RPM. After completion of the reaction, the reaction mixture was washed with deionized water until the metal ions could not be detected in the washing liquid, and then after filtration to get the CCR immobilized with metal ions. During the sulfonating, 15 mL H_2SO_4 solution (98%, w/v) was added drop wisely into a three-necked flask containing 2 g CCR at −5 °C under stirring. The reaction mixture was continuously stirred for 5 h at −5 °C after the addition was completed. Subsequently, 200 mL D.I. water was added into the flask and the mixture was filtered to get the final product, which was thoroughly washed by using D.I. water and dried in a vacuum oven at 60 °C for 8 h. This product was named as sulfonated cross-linked chitosan (SCCR) immobilized with metal ions.

2.3. FTIR spectroscopy

Fourier transform infrared spectroscopy (FTIR) was conducted using a NicoletiN10 FT-IR microscope (Thermo Nicolet Corporation, Madison, WI). The samples were pressed uniformly into a disc. The sample spectra were obtained in duplicates using an average of 64 scans over the range 4000–500 cm^{-1} with a spectral resolution of 8 cm^{-1} (Bian et al., 2014).

2.4. SEM analysis

The images of morphology and porous features of bamboo were observed by JSM-6700F (JEOL, Japan) scanning electron microscopy (SEM) operated at 20 kV accelerating voltage. Prior to imaging, the samples were sputter-coated with gold to make the fibers conductive, avoiding degradation and building up the charge of the specimen.