



Hydrolysis of cellulose into reducing sugars in ionic liquids



Xianxiang Liu^{a,b,*}, Qiong Xu^a, Junyi Liu^a, Dulin Yin^a, Shengpei Su^{a,*}, Hui Ding^a

^a National & Local Joint Engineering Laboratory for New Petro-Chemical Materials and Fine Utilization of Resources, Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education of China), College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, China

^b Department of Chemistry and Biochemistry, The University of Southern Mississippi, Hattiesburg, MS 39406, United States

ARTICLE INFO

Article history:

Received 3 August 2015

Received in revised form 26 September 2015

Accepted 30 September 2015

Available online 9 October 2015

Keywords:

Hydrolysis

Cellulose

Ionic liquids

Reducing sugar

Magnetic catalyst

ABSTRACT

An effective method was developed for the production of reducing sugars (RS) from the hydrolysis of cellulose over a magnetic acid catalyst. The sulfonation of the core-shell structured $\text{Fe}_3\text{O}_4@\text{C}$ with Fe_3O_4 as a magnetic core could generate the magnetic acid catalyst ($\text{Fe}_3\text{O}_4@\text{C}-\text{SO}_3\text{H}$). The hydrolysis of cellulose was performed under several crucial conditions. Hydrolysis of cellulose in ionic liquid 1-butyl-3-methyl imidazolium chloride ([BMIM]Cl) was greatly affected by the content of water. The highest RS yield and glucose selectivity were obtained in 72.1% and 82.5% at 110 °C after 3 h with the weight ratio of [BMIM]Cl to water being 20. It should be mentioned that this catalyst not only owns the high stability but also can be facile recovered by an external magnet.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Due to the increase in the need of petroleum-based resources for the production of chemicals and fuels, a great attention has been paid on the utilization of renewable resources as an alternative to fossil resources. In this regard, biomass is considered to be carbon neutral resources. The transformation of biomass into fuels and chemicals has captured an intense interest, which is coined as “biorefinery” [1–7]. Cellulose is the most abundant carbohydrates, and it consists of glucose units connected by β -1, 4-glycosidic bonds. The β -1, 4-glycosidic bonds in cellulose are strongly connected by the tight packing of cellulose chains in microfibrils. Therefore, cellulose almost shows no solubility most of the common solvents, which make it difficult to transformation of cellulose into value added chemicals [8]. In order to make full use of cellulose, hydrolysis of cellulose plays a crucial role in the effective utilization of cellulose [9,10].

Up to dates, several methods have been reported for the hydrolysis of cellulose, and some of them could afford satisfactory RS

yields and glucose selectivity. The hydrolysis conditions are generally mild for the cellulose hydrolysis over cellulases. But the activity of cellulases are inhibited is sensitive to inhibitors such as furfural and 5-hydroxymethylfurfural [11,12], and a low hydrolysis rate is usually observed. Hydrolysis of cellulose in supercritical water is carried out under harsh conditions (high temperature and high pressure). Although the hydrolysis rate is very fast, there are many side reactions under harsh conditions [13]. Acid promoted cellulose hydrolysis of cellulose is the most popular method for a long time. Mineral acids are effective to cut the β -1,4-glycosidic bonds, however, a lot of waste acid is released, and an extra waste treatment is required [14]. From the view point of green chemistry, hydrolysis of cellulose over heterogeneous catalysts has received a growing interest in these past decades, as it is relative easy to recover and reuse these heterogeneous catalysts [15]. Many kinds of heterogeneous catalyst were applied for the hydrolysis of cellulose, such as ion-exchange resin [16], heteropolyacids [17], sulfonated activated carbon [18].

Magnetic catalyst as a new kind of heterogeneous catalyst is popular in recent years, as recovery of the magnetic catalyst is facile to operate with an assist of an external magnet [19–22]. Recently, some authors claimed the hydrolysis of cellulose over magnetic acid catalysts [23]. In those reports, hydrolysis of cellulose is generally performed in water. As cellulose is insoluble in water, the β -1,4-glycosidic bonds in cellulose chain are resisted to be attacked by the acid sites of the heterogeneous catalysts. Ionic liquids [24], consisting of specific anions and cations, can dissolve cellulose by the

* Corresponding authors at: National & Local Joint Engineering Laboratory for New Petro-Chemical Materials and Fine Utilization of Resources, Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education of China), College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, China (X. Liu). Tel.: +86 731 88872238; fax: +86 731 88872531.

E-mail addresses: lixx@hunnu.edu.cn, xianxiang.liu@usm.edu (X. Liu), sushengpei@gmail.com (S. Su).

destroying the hydrogen bonds in cellulose. Thus, ionic liquids were proved to be a perfect solvent candidate for the functionalization of cellulose and hydrolysis of cellulose [25]. In the previous work reported by Xiong et al., they reported the hydrolysis of cellulose over a magnetic $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$ acid catalyst, in ionic liquid 1-butyl-3-methyl imidazolium chloride ([BMIM][Cl]) [26]. The $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$ catalyst was prepared by the sulfonation of silica coated Fe_3O_4 particles ($\text{Fe}_3\text{O}_4@\text{SiO}_2$). With the aim of development of sustainable chemistry in hand, it would be much more preferable to use the renewable resources to prepare the catalysts. Herein, in this work, a new heterogeneous $\text{Fe}_3\text{O}_4@\text{C-SO}_3\text{H}$ magnetic catalyst was used to hydrolyze cellulose in ([BMIM][Cl]). The out layer carbon was formed by the hydrothermal treatment of glucose in the presence of Fe_3O_4 nanoparticles. In addition, the as-prepared $\text{Fe}_3\text{O}_4@\text{C-SO}_3\text{H}$ catalyst was also effective in the hydrolysis of lignocelluloses (see Fig. 1).

2. Experiments

2.1. Materials

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (99.5%), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (99.5%) and glucose (99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Chlorosulfonic acid (99%), 1-chlorobutane (98%), cellulose (100%) and N-methylimidazole (98%) were purchased from Aladdin Chemicals Co., Ltd. (Beijing, China).

2.2. Catalysts preparation and characterization

Magnetic $\text{Fe}_3\text{O}_4@\text{C-SO}_3\text{H}$ catalyst was prepared according to the previous reported method [27]. As depicted in Fig. 2, $\text{Fe}_3\text{O}_4@\text{C}$ particles with Fe_3O_4 as the core were prepared by hydrothermal treatment of glucose in the presence of Fe_3O_4 . $\text{Fe}_3\text{O}_4@\text{C}$ was then treated with chlorosulfonic acid to give $\text{Fe}_3\text{O}_4@\text{C-SO}_3\text{H}$ catalyst. The amount of H^+ in the $\text{Fe}_3\text{O}_4@\text{C-SO}_3\text{H}$ catalyst was determined to be 1.40 mmol/g. Although the hydrothermal process could produce some weak acid groups such as $-\text{OH}$, $-\text{COOH}$, the acid used for the hydrolysis of cellulose should be catalyzed by $-\text{SO}_3\text{H}$ group.

2.3. Hydrolysis of cellulose

Cellulose (100 mg) was slowly added in [Bmim]Cl (2.0 g) at 100 °C with a high-speed stirring, and the mixture was stirred to give a clear solution. Then the magnetic $\text{Fe}_3\text{O}_4@\text{C-SO}_3\text{H}$ catalyst (60 mg) and water (100 mg) were added in the cellulose solution. The hydrolysis of cellulose was performed at 110 °C for 3 h. After reaction, the mixture was diluted with water to a certain concentration. The RS yields were obtained by the Imoto method [28].

2.4. RS analysis by Imoto method

Imoto reagent was prepared according to the known method, and stocked for one week before use [28]. Imoto reagent (0.5 mL) and the sample solution (4.5 mL) were mixed and subjected to be heated at 100 °C for 5 min. After cooling down to room temperature, determination of the absorbance of the solution was performed on UV-Vis spectrophotometer at 540 nm. The amount of the RS was obtained by the calibration of the standard curve.

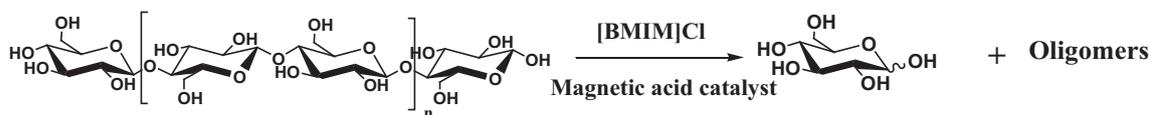


Fig. 1. Hydrolysis of cellulose into reducing sugars.



Fig. 2. Synthesis scheme of the $\text{Fe}_3\text{O}_4@\text{C-SO}_3\text{H}$ catalyst.

2.5. Analysis of hydrolysis products

The samples were firstly filtered with a 0.22 μm syringe filter prior to analysis by high-performance liquid chromatography (HPLC). The reducing sugars were analyzed by a Sugar-Pak-1 column and RI detector. Sulfuric acid aqueous solution (0.01 mmol L^{-1}) was used as the mobile phase at a flow rate of 0.6 mL min^{-1} .

3. Results and discussion

3.1. Hydrolysis of cellulose at different reaction temperatures

Initially, hydrolysis of cellulose was conducted in [BMIM]Cl at 110 °C, 120 °C and 140 °C, respectively, with the aim to investigate the reaction temperature on the hydrolysis of cellulose. Seeing from Fig. 3, the reaction temperature showed great influence on the RS yields. For the reaction temperatures of 110 °C and 120 °C, RS yields firstly increased to the highest points, and then it gradually decreased. Hydrolysis of cellulose at 110 °C afforded the maximum RS yield of 67.5% after 3 h, and the highest RS yield reached 64.8% after 2 h at the reaction temperature of 120 °C. When the reaction temperature was raised to 140 °C, a RS yield of 60.9% was achieved after a short reaction time of 1 h. According to these results, it can be concluded that the hydrolysis of cellulose was accelerated by the elevating of the hydrolysis of reaction temperature. For example, RS yield increased with an increase of the reaction temperature from 110 °C to 140 °C at the same reaction period of 1 h. The possible reason can be envisaged that molecules moved much more freely at higher reaction temperature, which accelerated the contact of β -1,4-glycosidic bonds of cellulose chain with the catalyst.

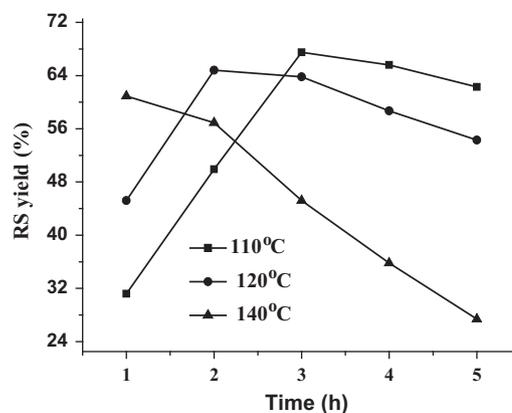


Fig. 3. The results of cellulose hydrolysis at different reaction temperatures. Reaction conditions: cellulose (100 mg), [BMIM]Cl (2.0 g), water (50 mg), $\text{Fe}_3\text{O}_4@\text{C-SO}_3\text{H}$ (60 mg).

Download English Version:

<https://daneshyari.com/en/article/205371>

Download Persian Version:

<https://daneshyari.com/article/205371>

[Daneshyari.com](https://daneshyari.com)