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Efficient conversion of cellulose into biofuel precursor 5-hydroxymethylfurfural in dimethyl sulfoxide–ionic liquid mixtures

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HIGHLIGHTS

- Conversion of cellulose into HMF was developed in DMSO catalyzed by $AlCl_3$.
- HMF yield of 20.5% was obtained from cellulose in DMSO.
- Ionic liquid [BMIM]Cl largely promoted the conversion of cellulose into HMF in DMSO.
- High HMF yield of 54.9% was obtained in a mixed solvent DMSO-[BMIM]Cl (10 wt.%).

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ABSTRACT

In recent years, cellulose has received increasing attention as a potential material for the production of biofuels and bio-based chemicals. In this study, a new process for the efficient conversion of cellulose into 5-hydroxymethylfurfural (HMF) was developed by the use of $AlCl_3$ as the catalyst in DMSO–ionic liquid ([BMIM]Cl) mixtures. Various reaction parameters such as reaction time, reaction temperature, solvent and catalyst dosage were investigated in detail. A high HMF yield of 54.9% was obtained from cellulose at 150 °C after 9 h in a mixed solvent of DMSO–[BMIM]Cl (10 wt.%). More importantly, the catalytic system could be reused for several times despite of the slight loss of its catalytic activity.

1. Introduction

The rapid development of human society requires much more energy and chemicals, and it is estimated to grow by more than 50% by 2025 (Ragauskas et al., 2006). However, the fossil fuels becomes shrinking gradually, which is the world's main source of energy and chemicals at present. This issue has prompted a direction to replace fossil fuels resources with renewable and sustainable resources (Espinosa et al., 2013; Greenhalf et al., 2013). Biomass is the only widely available carbon source apart from fossil resources. Thus, the abundant biomass is the unique renewable resources that can be converted into liquid fuels, and value-added chemicals through effective biorefinery routs (Grootscholten et al., 2013; Liu and Zhang, 2013). The majority (60–90 wt.%) of plant biomass is the biopolymer carbohydrates stored in the form of cellulose and hemicellulose. However, the structure of cellulose is highly crystalline, due to the presence of the extensive intra- and inter-molecular hydrogen bonds and Van der Waals interactions Nishiyama et al., 2003. The inert structure of cellulose makes it difficult to be accessed by other reagents. Therefore, it is still challenging to effectively convert cellulose into liquid fuels and valuable fine chemicals, due to its poor solubility in many conventional solvents such as organic solvents and water (Hidayat et al., 2012; Hundt et al., 2013).

Nowadays, one of the most attractive and promising approaches is to convert C6-based carbohydrates into 5-hydroxymethylfurfural (HMF) which have been recognized as important versatile platform compounds for the synthesis of a broad range of new products as well as for the replacement of fossil resources-derived fuels and chemicals (Scheme 1) (van Putten et al., 2013). HMF, which is formed from the dehydration of hexose, was first reported at the end of the 19th century. As shown in Scheme 1, HMF is simultaneously an aromatic aldehyde, an aromatic alcohol and a furan ring system. Thus, HMF has been called a "sleeping giant". As shown in Scheme 1, HMF can be used for the production of various chemicals and liquid fuels such as

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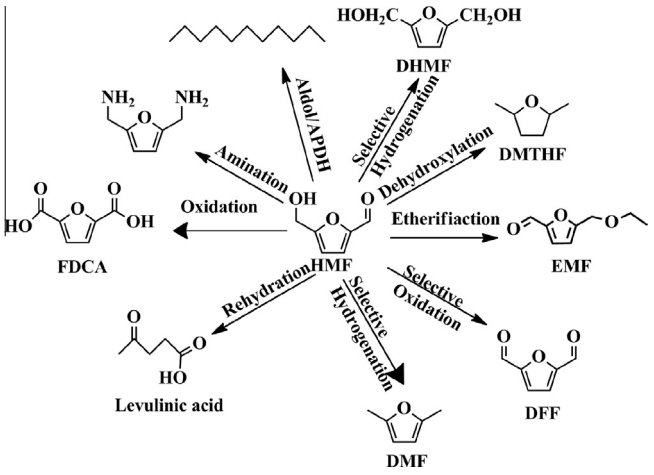

Scheme 1. Catalytic conversion of HMF into various chemicals and liquid fuels.

2,5-dihydroxymethylfuran (DHMF), 2,5-dimethylfuran (DMF), 2,5-dimethyltetrahydrofuran (DMTHF), 5-ethoxymethylfurfural, 2,5-diformylfuran (DFF), 2,5-furandicarboxylic acid (FDCA), levulinic acid (LA) and linear alkanes (Hu et al., 2012).

In the past decades, the dehydration of fructose and inulin has been reported using acid catalysts in the presence of water, organic solvents, ionic liquids and two-phase systems. Moderate to high HMF yields were obtained from fructose based carbohydrates (Zhu et al., 2011). However, it should be pointed out that fructose is not abundant and very expensive, which limits the large-scale and sustainable production of HMF from fructose. On the contrary, glucose has been considered as the preferred feedstock for the production of HMF, as it is the most abundant and the cheapest monosaccharide. However, synthesis of HMF from glucose due to the stable pyranoside ring structure of glucose. Therefore, there is a strong incentive to develop an efficient process for the production of HMF using glucose as starting material. A major breakthrough was developed by Zhao et al. (2007). They reported the conversion of glucose in ionic liquid [EMIM]Cl using $CrCl_2$ as catalyst, which gave a high HMF yield of 70%. Later, other metal salts such as $GeCl_4$, $SnCl_4$, and $ZrCl_4$ in ionic liquids also showed catalytic activity for the conversion of glucose into HMF (Hu et al., 2009; Stahlberg et al., 2010; Zhang et al., 2011).

Cellulose, which is made up of glucose unit via β-1,4-glycosidic bonds, is the most abundant carbohydrate in nature. Synthesis of HMF directly from cellulose is desirable for large-scale production of HMF because it can reduce the step of the production of glucose and the corresponding costs. However, the tight H-bond network and van der Waals interactions in cellulose makes it notoriously resistant to hydrolysis. In 2002, Seri et al. (2002) reported that catalytic conversion of cellulose by $LaCl_3$ in water at 250 °C could produce HMF with a low yield of 19%. Until recently, a significant attention has been paid to the transformation of cellulose into HMF in ionic liquids due to the excellent dissolvability of cellulose in ionic liquids (Swatloski et al., 2002). For instance, Su et al. (2009) reported the formation of HMF with 55.4% yield from cellulose using a combination of $CrCl_2$ and $CuCl_2$ in 1-ethyl-3-methylimidazolium chloride [EMIM]Cl. Later, other methods have also been developed for the conversion of cellulose into HMF catalyzed by $CrCl_3$ in ionic liquid (Tan et al., 2011; Zhang et al., 2010). However, in view of the toxicity and polluting characteristics of $CrCl_2$ or $CrCl_3$, some other Lewis acids with low toxicity such as $ZrCl_4$ (Liu et al., 2013) and $InCl_3$ (Li et al., 2013) have also been applied to catalyze the conversion of cellulose into HMF in ionic liquids. However, the high cost of ionic liquids makes them probably not suitable candidates for the economically large-scale synthesis of HMF. Therefore, it is strongly desired to completely or partially replace expensive ionic liquids with water or highly polar organic solvents for the economical and sustainable conversion of cellulose into HMF.

Recently, $AlCl_3$ with low toxicity was found to show high catalytic activity in the conversion of carbohydrates into HMF (Pagan-Torres et al., 2012; Yang et al., 2012). However, there was no report on the synthesis of HMF from cellulose using $AlCl_3$ as the catalyst in the cheap solvent systems. Herein, in the present work, we firstly report our results on the synthesis of HMF from cellulose catalyzed by $AlCl_3$ in a mixed solvent of DMSO and [BMIM]Cl (Scheme 2).

2. Experimental section

2.1. Methods

1-Butyl-3-methylimidazole chloride ([BMIM]Cl) was prepared according to our previous work (Zhang et al., 2009). Glucose was purchased from ABCR GmbH & Co. (Karlsruhe, Germany). Avicel PH-101 cellulose was purchased from Sigma (St Louis, USA). Acetonitrile (99.99%) was purchased from Tedia Co. (Fairfield, USA). HMF was purchased from Beijing Chemicals Co., Ltd. (Beijing, China). Dimethyl sulfoxide (DMSO) and $AlCl_3$ (99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All other chemicals were supplied by local suppliers and used without further purification.

2.2. Typical procedure for the catalytic conversion of cellulose into HMF

In a typical run, cellulose (100 mg) and $AlCl_3$ (8.2 mg) were added into a mixed solvent of DMSO (4.5 g) and [BMIM]Cl (0.5 g) in a 10 mL round-bottom flask equipped with a condenser. The reactor was then immersed into the preheated oil bath, and the reaction mixture was stirred at the speed of 600 rpm for a given reaction time. Time zero was recorded when the reactor was immersed into the preheated oil bath. After reaction, the reaction mixture was diluted with deionized water, and the solution was centrifuged at 10,000 rpm for 8 min. The clear liquid was further employed for product analysis.

2.3. Determination of the products

Quantitative analysis of HMF was performed by high-performance liquid chromatography (HPLC) method, using a reversed-phase C18 column (200 × 4.6 mm) and an ultraviolet detector at 280 nm. Acetic acid aqueous solution (1 wt.%) and acetonitrile with the volume ratio of 15:85 were used as the mobile phase at a rate of 1.0 mL/min, and the column oven temperature was maintained at 30 °C. The concentration of HMF was in samples was canculated based on the standard curve obtained with the standard substances.

3. Results and discussion

3.1. Catalytic conversion of glucose into HMF in DMSO by various Lewis acids

As glucose was the important intermediate for the one-pot conversion of cellulose, the catalytic conversion of glucose into HMF was initially carried out in DMSO in the presence of some common Lewis acids at 130 °C for 4 h. The blank experiment was carried out in DMSO without catalyst, and a negligible HMF yield was