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Zeolite-promoted transformation of glucose into 5-hydroxymethylfurfural in ionic liquid

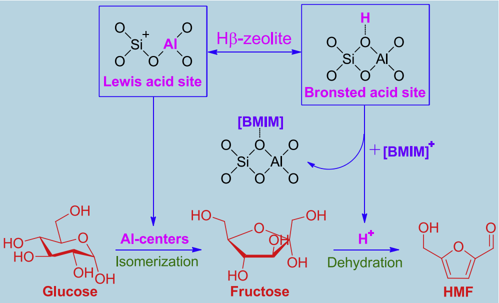
Lei Hu [a,b,*], Zhen Wu [a,b], Jiaxing Xu [a,b], Yong Sun [c], Lu Lin [c,*], Shijie Liu [d]

[a] *Jiangsu Key Laboratory for Biomass-based Energy and Enzyme Technology, Huaiyin Normal University, Huaian 223300, China*
[b] *School of Chemistry and Chemical Engineering, Huaiyin Normal University, Huaian 223300, China*
[c] *School of Energy Research, Xiamen University, Xiamen 361005, China*
[d] *Department of Paper and Bioprocess Engineering, State University of New York, College of Environmental Science and Forestry, Syracuse 13210, NY, USA*

HIGHLIGHTS

- Hβ-zeolite (Si/Al = 25) was very efficient for the conversion of glucose into HMF.
- The reaction kinetics was studied and determined to be first-order.
- Imidazolium cation and chloride anion of [BMIM]Cl had a synergistic effect.
- A plausible mechanism involving Lewis and Brønsted acid sites was proposed.
- Hβ-zeolite (Si/Al = 25) and [BMIM]Cl could be easily regenerated and recycled.

GRAPHICAL ABSTRACT



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ABSTRACT

A variety of zeolite catalysts were investigated for the conversion of glucose into 5-hydroxymethylfurfural (HMF) in ionic liquid 1-butyl-3-methylimidazolium chloride ([BMIM]Cl), and the results revealed that Hβ-zeolite with a unique BEA structure and a moderate Si/Al ratio of 25 possessed the highest catalytic activity, which resulted in 50.3% HMF yield with 80.6% glucose conversion at a reaction temperature of 150 °C for only 50 min. In the presence of Hβ-zeolite (Si/Al = 25) and [BMIM]Cl, the reaction kinetics for the conversion of glucose into HMF was studied and determined to be in accordance with a first-order reaction rate equation, and the activation energy and pre-exponential factor were 97.4 kJ mol^{-1} and 2.2×10^{10} min^{-1}, respectively. Moreover, a plausible mechanism involving the isomerization of glucose into fructose followed by the dehydration of fructose into HMF was proposed on the basis of the synergistic catalytic effect between Lewis acid sites and Brønsted acid sites of Hβ-zeolite. Hβ-zeolite (Si/Al = 25) could be easily regenerated via a simple calcination, and a similar HMF yield with the first reaction run was observed in the seventh reaction run. More importantly, Hβ-zeolite (Si/Al = 25) and [BMIM]Cl were also confirmed to be an excellent combination for the conversion of other carbohydrates such as fructose, sucrose, maltose, cellobiose, starch and cellulose into HMF.

1. Introduction

An ever increasing energy demand and diminishing fossil resources combined with growing concerns about global

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[*] Corresponding authors. Address: School of Chemistry and Chemical Engineering, Huaiyin Normal University, Huaian 223300, China (L. Hu). Tel.: +86 0517 83526983; fax: +86 0592 2880702.

E-mail addresses: hulei@hytc.edu.cn (L. Hu), lulin@xmu.edu.cn (L. Lin).

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warming and environmental pollution have made the efficient utilization of renewable biomass a pressing issue in both scientific and industrial communities [1–10]. Nature produces 170 billion metric tons of biomass per year by photosynthesis, 75% of which can be assigned to carbohydrates [11–13]. In recent years, the conversion of biomass-derived carbohydrates into 5-hydroxymethylfurfural (HMF), which is considered as a vitally important versatile intermediate that can be further transformed into a series of high-quality biofuels such as 2,5-dimethylfuran (DMF) [14], 5-ethoxymethylfurfural (EMF) [15], ethyl levulinate (EL) [16] and $C_9 \sim C_{15}$ alkanes [17] and high-value chemicals such as levulinic acid (LA) [18], 2,5-bishydroxymethylfurfural [19] and 2,5-diformylfuran (DFF) [20] and 2,5-furandicarboxylic acid (FDCA) [21], is a very promising pathway for the efficient utilization of biomass resources.

Among different types of carbohydrates, fructose is thought to be the ideal and optimal feedstock for the production of HMF, and excellent yields are readily obtained in various catalytic systems [22–28]. However, it should be pointed out that fructose is not abundant in nature and its cost is very high, which inhibit the practical production of HMF [29]. In contrast, glucose, the most abundant and the cheapest monosaccharide, has been increasingly regarded as a promising raw material for the production of HMF [30]. Disappointingly, satisfactory HMF yields are rarely obtained from glucose in the presence of water [31], organic [32] or mixed water-organic solvents [33], which can be attributed to a stable six-membered pyranoside structure of glucose [34]. Thus, the efficient conversion of glucose into HMF is still a challenge [5,12,13]. Ionic liquids, as green and powerful solvents with some specific properties, have been gradually used for the conversion of glucose into HMF. In 2007, an unprecedented HMF yield of nearly 70% was firstly achieved from glucose in ionic liquid 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) by the use of $CrCl_2$ [2]. Subsequently, other metal chlorides such as $CrCl_3$, $SnCl_4$ and $ZrCl_4$ were also successfully employed in various ionic liquids for the conversion of glucose, good yields of HMF ranging from 47.5% to 81% were obtained [35–38]. Although the above mentioned metal chloride catalysts are effective for the production of HMF from glucose, they possess some disadvantages including toxicity and separation problems.

More recently, many environmentally benign and easily separable solid acid catalysts such as $NA-p, TiO_2, ZrO_2, SO_4^{2-}/ZrO_2, SO_4^{2-}/ZrO_2-TiO_2, SO_4^{2-}/ZrO_2-Al_2O_3$ and HT/Amberlyst-15 were prepared and used for the conversion of glucose into HMF, which resulted in the moderate yields ranging from 10% to 51% [11,29,39–41]. Unfortunately, these catalytic systems need either very high reaction temperature (160–200 °C) or very long reaction time (180–540 min), which is unfavorable for the practical production of HMF.

According to the above mentioned research situations and existing problems, a more efficient process for the conversion of glucose into HMF using a commercial Hβ-zeolite with a unique BEA structure and a moderate Si/Al ratio of 25 as solid acid catalyst in relatively inexpensive ionic liquid 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) was developed in the present work, and various reaction parameters such as temperature, time, catalyst loading, glucose concentration and water content were optimized to obtain a higher HMF yield. In addition, the reaction kinetics and plausible mechanism for the conversion of glucose into HMF as well as the feasibility for the conversion of other carbohydrates such as fructose, sucrose, maltose, cellobiose, starch and cellulose into HMF in the presence of Hβ-zeolite (Si/Al = 25) and [BMIM]Cl were also detailedly studied.

2. Material and methods

2.1. Materials

HMF (99%), caprolactam (CPL, 99%) and tetraethyl ammonium chloride (TEAC, 99%) were purchased from Shanghai Energy Chemical Co. Ltd. (Shanghai, China). [BMIM]Cl (99%), 1-butyl-1-methylpyrrolidinium chloride ([BMPY]Cl, 99%), 1-butylpyridinium chloride ([BPY]Cl, 99%), 1-butyl-3-methylimidazolium acetate ([BMIM]OAc, 99%), 1-butyl-3-methylimidazolium terafluoroborate ($[BMIM]BF_4$, 99%) and 1-butyl-3-methylimidazolium hexafluorophosphate ($[BMIM]PF_6$, 99%) were supplied by Shanghai ChengJie Chemical Co. Ltd. (Shanghai, China). HY-zeolite, H-mordenite, Hβ-zeolite and HZSM-5 were purchased from Shanghai Novel Chemical Technology Co. Ltd. (Shanghai, China). Glucose, fructose, sucrose, maltose, cellobiose, starch, cellulose, dimethyl sulfoxide (DMSO), *N*,*N*-dimethyl acetylamide (DMA), *N*,*N*-dimethyl formamide (DMF), tetramethylene sulfone (TMS) and *N*-methyl pyrrolidone (NMP) were supplied by Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) and used without further purification.

2.2. Typical procedure for the conversion of glucose into HMF

The catalytic experiments were carried out in the tubular glass reactor of 18 mm × 138 mm with a lid, and all the zeolite catalysts were activated at 550 °C for 5 h before loading into the reactor, and each pre-set experiment was repeated three times. A typical procedure for the conversion of glucose into HMF is as follows: 100 mg glucose and 40 mg different zeolite catalyst were added into 1 g [BMIM]Cl. The reactor was then sealed and placed in an oil-bath at an elevated temperature of 140 °C and stirred at a speed of 500 rpm for 30 min. At the end of the reaction, the reaction mixture was immediately quenched to room temperature in an ice-water bath. Soon afterwards, 4 mL deionized water was added to the reaction mixture, which was centrifuged at 10,000 rpm for 5 min, and then, a single liquid layer was formed.

2.3. Catalyst characterization

The total acid densities of zeolite catalysts were determined by NH_3-TPD method, which was performed on a Micrometeritics Autochem II 2910 instrument. Typically, the dried zeolite catalysts were placed in a quartz reactor and pretreated in flowing He at 550 °C for 1 h. Subsequently, the temperature was cooled to 100 °C and the samples were subjected to anhydrous NH_3 for 30 min. After NH_3 adsorption, the samples were flushed with He at 100 °C for 60 min and the desorption was carried out in a flow of He at a heating ramp of 10 °C min^{-1} to 650 °C. The acid properties of zeolite catalysts were detected by FT-IR spectroscopy of adsorbed pyridine on a Bruker spectrometer equipped with a MCT detector at a resolution of 4 cm^{-1}. Prior to the measurements, the dried zeolite catalysts were pressed in self-supporting discs and pretreated in vacuum at 400 °C for 4 h. After cooling down to room temperature, the samples were saturated with pyridine for 30 min and further evacuated at 200 °C for 30 min. And then, the amounts of adsorbed pyridine were calculated by the reported molar extinction coefficient [42]. The BET surface areas of zeolite catalysts were measured by Micromeritics Tristar II 3020 analyzer using a multipoint method on the basis of nitrogen adsorption–desorption isotherms at −196 °C.

2.4. HPLC analysis

HMF and glucose in the single liquid layer were analyzed using HPLC method on an Waters 2695 Separation Module equipped