

# Properties and catalytic activity of magnetic and acidic ionic liquids: Experimental and molecular simulation



Cunshan Zhou<sup>a,b,c,d</sup>, Xiaojie Yu<sup>a</sup>, Haile Ma<sup>a,b,c,\*</sup>, Xingyi Huang<sup>a</sup>, Henan Zhang<sup>a</sup>, Jian Jin<sup>a</sup>

<sup>a</sup> School of Food and Biological Engineering, Jiangsu University, 301 Xuefu Road, Zhenjiang 212013, China

<sup>b</sup> Jiangsu Provincial Research Center of Bio-process and Separation Engineering of Agri-products, Jiangsu University, 301 Xuefu Road, Zhenjiang 212013, China

<sup>c</sup> Jiangsu Provincial Key Laboratory for Physical Processing of Agricultural Products, Jiangsu University, 301 Xuefu Road, Zhenjiang 212013, China

<sup>d</sup> Heddle Initiative Research Unit, Advanced Science Institute, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

## ARTICLE INFO

### Article history:

Received 22 November 2013

Received in revised form 14 January 2014

Accepted 21 January 2014

Available online 31 January 2014

### Keywords:

Catalytic activity

Recyclability

Platform chemical

Dual functional ionic liquids

Molecular dynamics

## ABSTRACT

The exploitation of dual functional magnetic and acidic ionic liquids (MAILs) for hydrolysis of cellulose to platform chemicals can solve some practical challenges through easy separation of products and efficient catalyst recyclability. In this work, seven  $C_n\text{mim}/\text{FeCl}_4$  MAILs were synthesized and investigated with combined experimental and molecular dynamics. The MAILs contained  $\text{FeCl}_4^-$  anions and exhibited a typical hard magnetic materials behavior with rather strong magnetic susceptibilities. These MAILs were stable up to 250–310 °C, the decomposition was started up at 250/310–480–810 °C in two steps with the formation of the undecomposed residue. The Gibbs energy for the reaction of glucose/xylose conversion to 5-hydroxymethylfurfural by metal chlorides in the  $C_n\text{mimCl}$  ionic liquid was studied using the density functional theory calculations and the results that  $C_3\text{mim}/\text{WCl}_6$  may be the most hopeful catalyst. The MAILs have the potential to open up promising new catalytic systems because of their easy product separation and efficient catalyst recyclability.

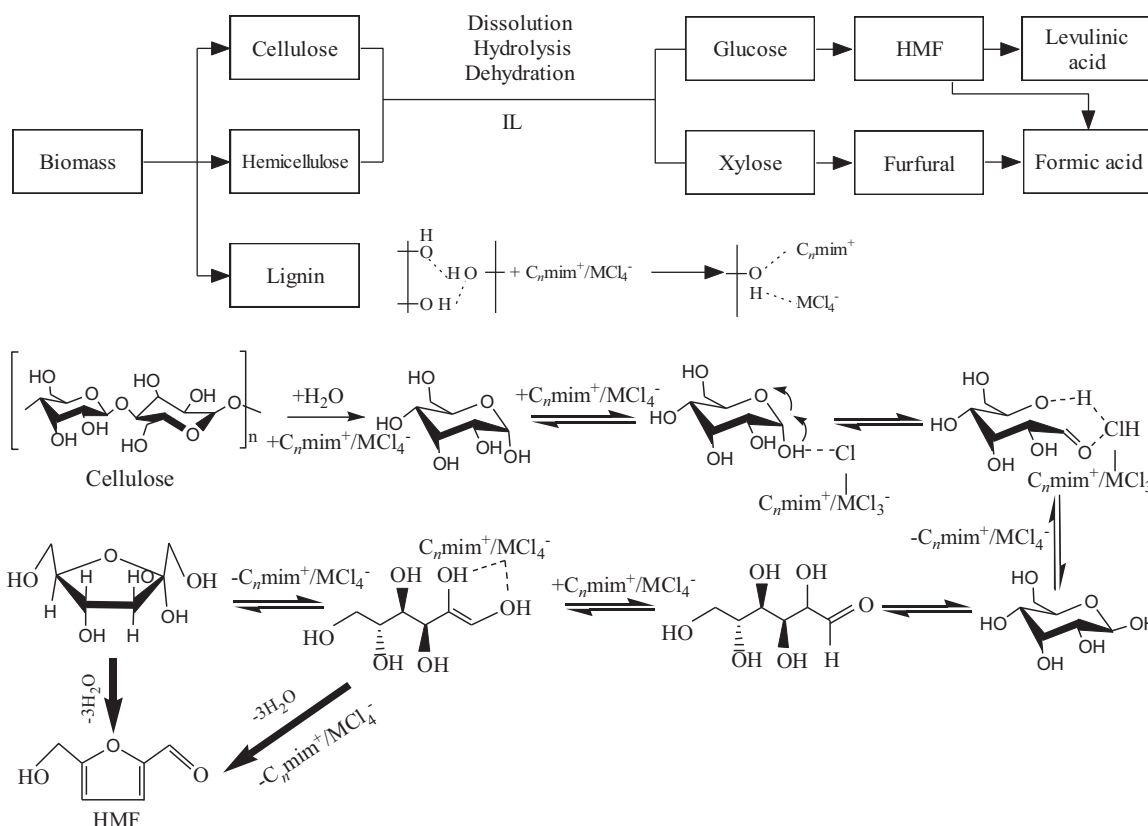
© 2014 Elsevier Ltd. All rights reserved.

## 1. Introduction

The exploitation and usage of fossil fuel is widely thought to be the cause of serious problems such as, climate anomalies (Friedlingstein & Solomon, 2005). Reserves of fossil fuels will eventually disappear and this will lead energy crisis (Shafiee & Topal, 2005). To prevent the imminent problems, alternative biofuels have been explored and successful stories such as first-generation biofuels from corn and soybean edible oil have confirmed the practical feasibility of biomass-to-biofuel (edible oil to gasoline) conversion. However, with the use of dependent survival agricultural and edible products and in this choice may create their own fatal problems such as food supply shortages as the world population grows and social issues (Godfray et al., 2010). Another option is typical and important chemical alternatives such as second-generation biofuels, feedstocks and platform chemicals produced from non-edible lignocellulosic biomass from agricultural waste (which has attracted most attention to date). Since considered and recognized as a particularly attractive option owing to its potential greener, and sustainability and carbon neutrality (Scheme 1) (Nel & Cooper, 2009). Until now, a great deal of work has been carried on the

hydrolysis of cellulose with cellulases, mineral acids and solid acids. Enzymatic hydrolysis of cellulose is rather effective, but the reaction is sensitive to environmental contaminants, and suffers from inefficiency and a high enzyme cost (Engel et al., 2010; Salvador et al., 2010). Mineral acids have been comprehensively investigated to catalyze the degradation of cellulose at a variety of acid concentrations, high temperatures (180–250 °C) and high pressure. Furthermore, as far as safety and green concerned, degradation of the resulting glucose and some intermediates becomes an issue at such high temperatures. Meanwhile, large-scale use of mineral acid suffers from several related problems such as reactor corrosion, catalyst recovery/reuse and requires treatment of the waste, producing lots of pollution (Torget et al., 2000). The catalytic hydrolysis of cellulose into glucose with solid acids has the advantage of avoiding some of the above shortcoming owing to the ease of catalytic separation, recyclability and reduced damage to the corrosion (Shimizu & Satsum, 2011). Significant progress of this catalytic conversion has been made by using various types of particles acids with large pore size and super acid strength. As far as the real biomass feedstock and practical process for the hydrolysis of cellulose to glucose is concerned, challenges still exist for the solid acids catalytic system (Xu et al., 2011; Lange et al., 2012). Solid acids catalysts cannot be directly separated when residues are formed as solid power in the reaction process. Additionally, several important aspects also need to be looked at, and such as economic feasible, simplicity to

\* Corresponding author. Tel.: +86 511 88790958; fax: +86 511 88780201.  
E-mail address: [mhl@ujs.edu.cn](mailto:mhl@ujs.edu.cn) (H. Ma).



**Scheme 1.** Possible dissolution mechanism of cellulose in  $C_n\text{mim}^+/\text{MCl}_4^-$  MAILs and conversion of cellulose to HMF catalyzed with  $C_n\text{mim}^+/\text{MCl}_4^-$  MAILs ( $n=4, 6, 8, 10, 12, 14, 16$ ).

enlarge, efficiency and environmental green (Huang & Fu, 2013). Overall, economic, environmental, and sustainable aspects should be of concern when designing new catalytic systems.

Ionic liquids (ILs) have gained enormous attention in the past 30 years. They are solvents and are often regarded as “green”, “designable”, “friendly”, “non-coordinating” etc., nevertheless it is increasingly recognized that none of these tags could be used easily. Yet, considerable research in ILs green chemistry is still learned by trial-and-error method rather than fundamental principle of understanding and reasonable design. Not enough is known to date about properties and structures of these new materials in the liquid phase nor are all observed differences in reaction outcomes as compared to “conventional” solvents explained satisfactorily (Zhou, Yu, Ma, He, & Vittayapadung, 2013a; Zhou et al., 2013b). Recently, ILs have attracted more and more attention and have been utilized as catalysts for the hydrolysis of lignocellulosic biomass. The first mention of the dissolution of cellulose in an ILs was in 1934, but the utilization of ILs in the lignocellulose biofuel conversion only started from 2000 as a result of the energy crisis. In many of the possible biomass based chemicals, 5-hydroxymethylfurfural (HMF) is derived from dehydration of saccharides, such as pentose, hexose, sucrose, cellulose and inulin, and is considered as a pivotal building block in biomass biorefinery because it can derive a variant of beneficial derivatives, including 2, 5-dimethylfuran, which is a hopeful biofuel, 2, 5-diformylfuran, 2, 5-furandicarbaldehyde and 2, 5-furandicarboxylic acid (Zakzeski et al., 2010). Catalytic dehydration of pentose (fructose) to HMF making use of both homogeneous and heterogeneous catalytic reaction systems has been investigated extensively (Nishiyama et al., 2002). Notwithstanding the conversion of fructose to HMF without catalysts, higher yields of HMF have been realized with many catalysts, such as ion-exchange resins, ionic liquids, zeolites, and metal halide. In 2007, Zhao et al.

(Zhao, Holladay, Brown, & Zhang, 2007) discovered that  $\text{CrCl}_2$  in [EMIM]Cl (1-ethyl-3-methylimidazolium chloride; an imidazolium type ionic liquid) can efficiently catalyze the conversion of glucose to HMF.

Despite all the researches carried out in this area, there is little explanation on the reaction mechanism for the glucose/fructose conversion to HMF. Especially, glucose/fructose degradation in ionic liquid/metal halide catalysts remains poorly understood mechanistically, although somewhat experimental results have confirmed the essential nature of Cr species and the coordination characteristics of the complex between metal salts and sugars (Hu et al., 2009). However, in a recent DFT computations combined with EXAFS study, a transient binuclear Cr(II) species was reported to be in charge of the glucose/fructose isomerization necessary step (Pidko, Degirmenci, van Santen, & Hensen, 2010).

Magnetic 1-butyl-3-methylimidazolium tetrachloroferrate ( $\text{bmim}/\text{FeCl}_4$ ) was synthesized and first reported by Hayashi et al. (Hayashi, Saha, & Hamaguchi, 2006), but they did not mention the acidic property of the tested ILs at the same time in the paper. It would be extremely interesting and necessary to investigate the macroscopic and microscope responses of those multifunctional ionic liquids to a magnet in quantitative ways. Magnetic and acidic ionic liquids (MAILs) not only have the excellent properties of conventional ionic liquids, such as wide liquid range, higher ionic conductivity, excellent solubility, thermal stability and designability by appropriate modifications of cations or anions in structures, but also exhibit an unexpectedly strong response to an additional magnetic field and acidic catalytic activity. These properties make MAILs have more advantages and potential application prospects than conventional ILs in the fields of catalytic reactions (Wang et al., 2011; Misuka et al., 2011), solvent effects (Kim et al., 2008) and separation processes (Pei et al., 2010; Wang et al., 2010).

Download English Version:

<https://daneshyari.com/en/article/1386065>

Download Persian Version:

<https://daneshyari.com/article/1386065>

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