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Conversion of cellulose to HMF in ionic liquid catalyzed by bifunctional ionic liquids

Lilong Zhou, Runjuan Liang, Zhanwei Ma, Tinghua Wu *, Ying Wu *

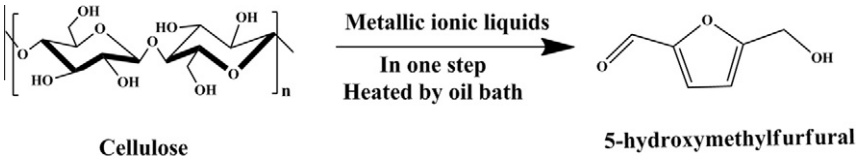
Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, Institute of Physical Chemistry, Zhejiang Normal University, Jinhua 321004, PR China

HIGHLIGHTS

- Cellulose is converted to HMF in yield of 53% on special catalysts in [BMIM]Cl.
- A bifunctional catalyst was designed in this work.
- This catalysis system can be recycled for many times.

GRAPHICAL ABSTRACT

Conversion of cellulose to HMF in ionic liquid catalyzed by metallic ion–acid functional ionic liquid.



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ABSTRACT

A new kind of bifunctional ionic liquid catalysts was synthesized to degrade microcrystalline cellulose in [BMIM]Cl at atmospheric pressure. The effects of reaction temperature, amount of catalysts, reaction time, ionic liquid purity and cellulose concentration on conversion were investigated. At low temperature cellulose can be degraded with being heated in [BMIM]Cl by oil bath. Among the as-synthesized catalysts, $Cr([PSMIM]HSO_4)_3$ exhibited the best performance. The HMF yield of 53% and TRS yield of 94% can be achieved at 120 °C in [BMIM]Cl for 5 h over 0.05 g $Cr([PSMIM]HSO_4)_3$/2.0 g [BMIM]Cl with 95% cellulose conversion.

1. Introduction

With fossil resources dwindle day by day, the development of alternative resources becomes a hotspot in chemical research field. The effective conversion of cellulose which is the most abundant biomass and composed by glucose unites through β-1, 4-glucosidic bonds attracts much attention in recent years. However, cellulose cannot be dissolved in traditional solvents such as H_2O, ethyl acetate, acetonitrile, aether (Notley et al., 2004; Rinaldi and Schüth, 2009). Therefore it's hard to be converted into other useful chemicals. Imidazole ionic liquids are a new kind of cellulose solvents (Swatloski et al., 2002). It makes conversion of cellulose to chemicals under homogeneous conditions at atmosphere pressure and low temperature become possible. As one of the main products of cellulose's degradation, HMF has several different functional groups. Therefore, it is considered as a potential platform chemical in the future. It can be converted to 2,5-dimethylfuran which is a biofuel just like gasoline and other important molecules such as levulinic acid, 2,5-furandicarboxylic acid, 2,5-diformylfuran, dihydroxymethylfuran and 5-hydroxy-4-keto-2-pentenoic acid (Rosatella et al., 2011).

Li et al. hydrolyzed different kinds of lignocellulose (corn stalk, straw, pine wood, bagasse) in [BMIM]Cl with mineral acid catalysts at 100 °C, and the yield of total reducing sugars (TRS) were 66%, 74%, 81% and 68%, respectively (Li and Zhao, 2007). Besides, they also treated different kinds of lignocellulose (wood chips of giant redwood, spruce and southern pine) with catalytic amount of hydrochloric acid in [AMIM]Cl. It was found that cellulose and hemicellulose were almost completely depolymerized, but lignin was only partly degraded (Li et al., 2008). Sievers et al. hydrolyzed loblolly by CF_3COOH in [BMIM]Cl (Sievers et al., 2009). Several

Abbreviations: HMF, 5-hydroxymethylfurfural; TRS, total reducing sugar; MCC, microcrystalline cellulose; AFIL, acid functional ionic liquid; BFIL, bifunctional ionic liquid.

* Corresponding author. Address: Institute of Physical Chemistry, Zhengjiang Normal University, 688 Yingbin Road, Jinhua 321004, PR China. Tel.: +86 0571 82283907.

E-mail addresses: thwu@zjnu.cn (T. Wu), yingwu@zjnu.cn (Y. Wu).

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