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Ionic liquid with metal complexes: An efficient catalyst for selective dehydration of fructose to 5-hydroxymethylfurfural

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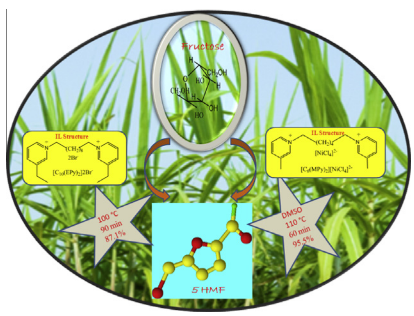
HIGHLIGHTS

- 95.5% Yield of HMF was obtained in mild condition by the dehydration of fructose.
- Ionic liquid containing transition metal complexes used as catalysts.
- Transition metal complexes have a remarkable effect on the dehydration of fructose.
- First example of IL with metal complexes in fructose dehydration.

GRAPHICAL ABSTRACT



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ABSTRACT

The dehydration of D-fructose has been studied with different kinds of pyridinium based dicationic ionic liquids as catalyst. The results showed that 1,1′-hexane-1,6-diylbis (3-methylpyridinium) tetrachloronickelate (II) $[C_6(Mpy)_2][NiCl_4]^{2-}$ in DMSO and 1,1′-decane-1,10-diylbis (3-ethylpyridinium) dibromide $[C_{10}(Epy)_2]2Br^-$ without DMSO have high catalytic activity. Highly efficient and selective dehydration of D-fructose to 5-hydroxymethylfurfural (HMF) was achieved in dimethyl sulfoxide (DMSO) under mild conditions with a fructose conversion of 95.6% and 95.5% HMF yield was achieved in 60 min reaction time at 110 °C and 87.1% yield obtained from $[C_{10}(Epy)_2]2Br^-$ without DMSO at 100 °C in 90 min reaction time. The ionic liquids used in this study will benefit many biofuel-related applications.

1. Introduction

High worldwide demand for energy, souring prices of petroleum, and concern over global climate change has led to resurgence in the development of alternative energy that can displace fossil transportation fuel. Biomass is one of the important renewable sources for securing future energy supply, production of fine chemicals and sustainable development. Current biomass resources comprise primarily industrial waste materials such as sawdust or pulp process wastes, hog fuel, forest residues, clean wood waste from landfills, and agricultural prunings and residues from plants such as lignocellulosic materials [1–10]. Recently, efforts have been devoted to the conversion of biomass into 5-hydroxymethylfurfural (HMF), a versatile and key intermediate to the production of high value polymers such as polyurethanes and polyamides, as well as for biofuels [2,11–13]. Number of catalysts has been reported in the literature for dehydration of sugars to HMF. However, most of them also promote side reactions that form undesired byproducts, and rehydrate HMF to form levulinic acid and formic acid [14–18]. HMF production is currently still facing significant technical challenges to make it economically feasible in an industrial scale. A simple and an efficient method to produce pure HMF from abundant renewable carbohydrates in high yield at low energy cost must be developed before a biorefinery platform can be built on the basis of this substrate [2,19,20].

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Sugar molecules are potential feedstock for this purpose. According to the literature, the use of metal chlorides in ionic liquid [EMIm]Cl have been found to be effective catalyst for converting sugars such as fructose and glucose to HMF. It was found that ionic liquid mediated catalysis by chromium is the successful catalytic transformation of fructose and glucose to 5-HMF. These results suggest that ionic liquids as solvents or catalysts can play a positive role in the development of effective processes for the dehydration of hexose to HMF [16]. Recently, we have reported that the synthesis of pyridinium based dicationic ionic liquids. Some of them used as catalysts for reaction such as esterification [21], carbonyl compounds reduction [22]. Ionic liquid containing transition metal complex $[C_6(Mpy)_2][NiCl_4]^{2-}$ (bulk as well as nanofiber composites) showed an excellent catalytic activity for hydrogen generation and nitroarenes reduction reactions [23–25]. We have used IL containing transition metal complex in multidisciplinary research (Fig. 1). As an extension of our ongoing studies of these ionic liquids, we report herein their application as catalysts for the dehydration of D-fructose to HMF. The ionic liquids used in this study will benefit for many biofuel-related applications.

So far many researchers were used ionic liquid as solvent and metal chlorides or other additives as catalyst for the dehydration of D-fructose [26–29]. Though ionic liquids played a major role in the dehydration of D-fructose, but it was used in large amounts which are lack of economical point of view. Recently, Xinlin Tong et al., studied the catalytic amounts of Brønsted-acidic ILs in water and organic solvents, which revealed the unique catalytic performance of ILs [30]. In this work, we used catalytic amount of different kinds of pyridinium dicationic ionic liquids with dimethyl sulfoxide (DMSO) and without DMSO. Dicationic with tetrachloronickelate (II) anion ($[C_6(Mpy)_2][NiCl_4]^{2-}$), itself has metal chloride, so additions of any additives are not required. They have shown good performance and gave excellent yield for 5 HMF than the previous reported works (Scheme 1). To the best of our knowledge, it is the first report for the dehydration of D-fructose to 5 HMF in ionic liquid containing metal chloride anion.

2. Experimental

2.1. Materials

All chemicals were purchased from sigma aldrich and used as received. Ionic liquids used in this study were synthesized according to our previous reported work [21,23].

2.2. Analysis

For analysis of solutions, water high performance liquid chromatography system equipped with UV detector (PAD-2996, 284 nm, XBridge™ C18 column (4.6 mm × 150 mm)) was employed. Mobile phase was a 5 mM sulfuric acid in 20% MeOH with a flow rate of 0.6 ml/min.

Fructose conversion (*X*), product yield (*Y*) and product selectivity (*S*) are defined as follows

$$X = \left(1 - \frac{\text{Fructose concentration in the product}}{\text{Fructose concentration in the loaded sample}}\right) \times 100\%$$

$$Y = \left(\frac{\text{Moles of 5 HMF formed}}{\text{Initial moles of fructose}}\right) \times 100\%$$

$$S(\%) = \frac{\text{Yield of product}}{\text{Fructose conversion}}$$

2.3. Typical procedure for the dehydration of D-fructose

An equivalent mixture of ionic liquid and fructose was used in the reaction. A typical procedure for the dehydration of D-fructose in $[C_6(Mpy)_2]\ [NiCl_4]^{2-}$ and $[C_{10}(Epy)_2]\ Br_2^-$ is as follows: D-fructose (0.36 g, 0.002 mol), $[C_6(Mpy)_2]\ [NiCl_4]^{2-}$ (1 g, 0.002 mol) and 5 ml DMSO; D-fructose (0.5 g, 0.003 mol), $[C_{10}(Epy)_2]\ Br_2^-$ (1.5 g, 0.003 mol) solutions are charged into a separate round bottom flask equipped with a magnetic stirrer and a condenser. The experiments were carried out in the oil bath at 110 °C and 100 °C respectively. After the reaction each sample was diluted with 10 ml of distilled water before analysis. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 3.333 (d, 1H), 4.658 (s, 2H), 6.468–6.477 (d, 1H, *J* = 3.6), 7.173–7.182 (d, 1H, *J* = 3.6), 9.509 (s, 1H); ^{13}C NMR (400 MHz, DMSO-d_6): δ_H (ppm) 177.873, 161.283, 152.033, 123.441, 110.012, 57.186

2.4. Typical separation procedure for 5 HMF

1,1′-Hexane-1,6-diylbis (3-methylpyridinium) tetrachloronickelate (II) ($[C_6(Mpy)_2]\ [NiCl_4]^{2-}$): After the reaction, the reaction mixture was transferred into a flask and was distilled under reduced pressure. The remaining mixture was extracted with ethyl acetate (10 ml × 10) after water (5 ml) was added, and then the organic phase was collected. After drying with anhydrous Na_2SO_4, the solvent evaporated by rotary evaporator to obtain pure HMF.

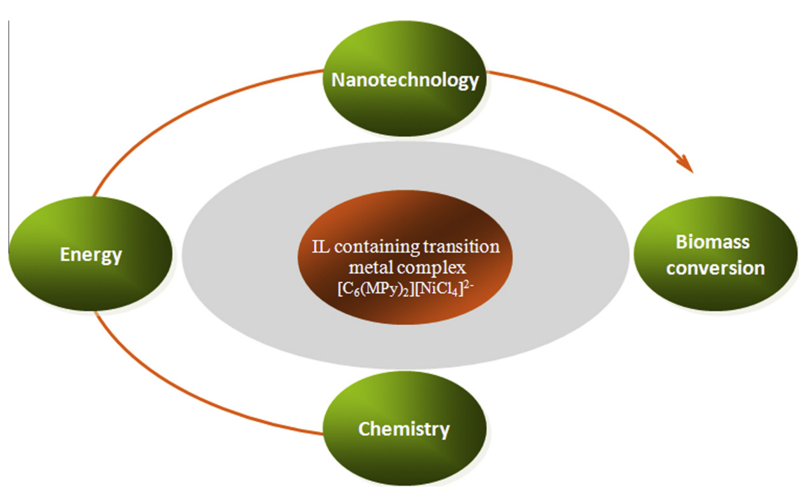

Fig. 1. Ionic liquid containing transition metal complex in multidisciplinary research [23–25].