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CONVERSION OF SUGARS INTO 5-HMF

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ABSTRACT

At present, fossil fuels are playing the major role to meet the energy requirements of the world. The large consumption of fossil fuels creates so many environmental problems, such as green-house gases have motivated the search for alternative, renewable fuel options. Biomass is one of the few resources that have the potential to meet the challenges of sustainable and green energy systems. 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. There are already a considerable range of chemical building blocks derived from renewable resources. Among them, 5-hydroxymethylfurfural (HMF) is a versatile platform chemical for the synthesis of a wide range of industrially important materials, including biofuels.

Keywords: *Biomass; Ionic liquids; 5-HMF; Sugars*

1. INTRODUCTION

Biomass energy generates far less air emissions than fossil fuels. Renewable energy is one of the most efficient ways to achieve sustainable development. Biomass has been used to meet the needs of civilization since prehistory. Several biomass chemical products can be traced to a time when neither the chemical mechanistic transformation process nor the chemical identities of the product were understood. If one considers the possible downstream chemical processing technologies, the conversion of sugars to value-added chemicals is very important. Hexoses are the six-carboned carbohydrates and are the most

abundant monosaccharide existing in nature. Among them d-fructose and glucose are economical and suitable to be used as the chemical feedstocks [1-4].

2. SYNTHESIS OF 5-HYDROXYMETHYLFURFURAL

Already numerous valuable chemicals are derived from renewable resources, among these HMF, plays a vital role, because it can be obtained from carbohydrates (sucrose, glucose, fructose and cellulose). HMF is a versatile platform chemical for the synthesis of a wide range of industrially important materials, including biofuels. It is a good starting point for the synthesis of precursors of pharmaceuticals, thermoresistant polymers, and macrocyclic compounds, and particularly for the synthesis of dialdehydes, ethers, amino alcohols, and other organic intermediates. Synthesis of HMF from sugars with economical and efficient routes at mild conditions is a challenging topic of great importance [5-7].

3. GLUCOSE TO 5-HMF

In this section, we focus few examples of 5-HMF produced from glucose by different catalyst reported in the literature. Notably, the use of acidic porous solid materials as catalyst is highly attractive due to the potential for combined acidic catalysis and shape-selective catalysis [8]. Jiménez-Morales et al. have investigated the production of 5-HMF using various catalysts based on mesoporous MCM-41 silica containing ZrO₂; they reported that these catalysts were quite selective toward 5-HMF, with only 5-HMF detected as product, while levulinic acid and formic acid were absent [9]. Xu et al. developed a series of ordered mesoporous zirconium oxophosphates for the dehydration of fructose to 5-HMF, with M-ZrPO-0.75 leading to 97.4% fructose conversion and 79.6% selectivity for 5-HMF when using dimethyl sulfoxide as reaction solvent under relatively mild conditions [10]. Mondal et al. employed the nanoporous sulfonated polymer SPPTPA-1 with very high surface acidity for the direct conversion of sugars to 5-HMF, and attained 51.4% 5-HMF yield from sucrose [11]. Furthermore, the enhancement effect of inorganic microporous materials on the production of 5-HMF has also recently been demonstrated. Swift et al. investigated tandem glucose isomerization and fructose dehydration to 5-HMF over the bifunctional aluminosilicate zeolite BEA

[12]. Furthermore, organic structure-directing agent (OSDA)- free zeolite beta with high Al content exhibited high catalytic performance in the conversion of glucose to HMF, with about 68% HMF yield obtained [13]. In recent years, ionic liquids have undergone a remarkable process of evolution for carbohydrates conversion. The IL, 1-hydroxyethyl-3-methylimidazolium tetra- fluoroborate ($[C_2OHMIM]BF_4$), was used a catalyst rather than as a solvent in the conversion of fructose or glucose to 5-HMF.

With glucose, the yield of 5-HMF reached as high as 67.3% after 1 h at 180 °C in dimethylsulfoxide (DMSO) as solvent [14]. Jadhav et al., was used zeolite (H-ZSM-5) as catalyst and butylmethylimidazolium chloride ($[Bmim]Cl$) as solvent, leading to a 45% yield of HMF [15].

4. FRUCTOSE TO 5-HMF

5-Hydroxymethyl-2-furaldehyde (HMF) is a key bio-based platform for the production of renewable monomers and bio-fuels. However, most of its syntheses are carried out under not sustainable conditions. Antonetti and co-workers [1'] reported the production of HMF from fructose and inulin, it was investigated following the Green Chemistry principles, adopting aqueous medium, appreciable substrate concentration (10 wt%), low loading of heterogeneous acid catalyst (niobium or zirconium phosphate) and microwave heating. Both the catalysts resulted very active and promising, in particular zirconium phosphate and the performances were related to their different acid characteristics. The optimization of HMF synthesis with zirconium phosphate was also supported by a statistical modelling, which shows that the highest yield to HMF (about 40 mol%) is ascertained at high temperature (190 °C) and short reaction time (8 min). The catalysts resulted recyclable maintaining their starting activity almost unchanged [16]. R. Kourieh et al was studied the catalytic dehydration of fructose and its conversion to 5-hydroxymethylfurfural was studied using tungstated zirconia oxides, with various tungsten oxide loadings (1–20 wt.%). The samples were prepared by incipient wetness impregnation and thoroughly characterized using a combination of different techniques: structural, thermal and calorimetric analyses. Zirconia was predominantly present in the investigated samples in the tetragonal phase when the WO_3 loading was above 10 wt.%. The samples exhibited amphoteric characteristics, as they adsorbed both ammonia and

sulfur dioxide on their surface. The number of surface acid sites increased with increasing WO₃ content. Fructose dehydration tests evidenced the formation of 5-hydroxymethylfurfural and by-products (formic and levulinic acids) [17]. The dehydration of D-fructose has been studied with different kinds of pyridinium, imidazolium based dicationic ionic liquids with symmetry and unsymmetry. In our group, we reported that 1,10-hexane-1,6- diylbis(3-methylpyridinium) tetrachloronickelate(II) [C₆(MPy)₂][NiCl₄]²⁻ in DMSO and 1,10-decane-1,10-diylbis(3-ethylpyridinium) dibromide [C₁₀(EPy)₂]2Br⁻ without DMSO have high catalytic activity towards fructose dehydration. A fructose conversion of 95.6% and 95.5% HMF yield was achieved by [C₆(MPy)₂][NiCl₄]²⁻ in 60 min reaction time at 110 °C and 87.1% yield obtained from [C₁₀(EPy)₂]2Br⁻ without DMSO at 100 °C in 90 min reaction time [7]. In 2012, we reported bis(Nmethylimidazolium) cations containing short oligo ethylene glycol linkers and mesylate (CH₃SO₃) anions based ILs (in catalytic amount) for sugar dehydration reactions. As a result, 92.3% of HMF yield was obtained from fructose in 40 min with one equivalent of [tetraEG(mim)₂][OMs]₂ at 120 °C. While, 67.2% of HMF was achieved from dehydration of sucrose at 120 °C in 150 min using two equivalents of [tetraEG(mim)₂][OMs]₂. Among those dicationic RTILs, [tetraEG(mim)₂][OMs]₂ RTIL was observed to be the most efficient catalyst, demonstrated by its ability to achieve 100% conversion and highest yield of HMF [18]. In 2014, we reported the synthesis of unsymmetrical dicationic ILs, imidazolium, pyridinium, and triethyl ammonium as cationic moiety and HSO₄, CH₃SO₃, and Br⁻ as an anionic moiety. The newly synthesized all unsymmetrical ILs were tested for dehydration of fructose into 5-hydroxymethylfurfural (HMF) in mild reaction conditions. Especially ([tetraEG(mim)(triethylamo)]HSO₄) unsymmetrical IL was showed higher catalytic activity among all synthesized ILs, it exhibited 100% consumption of fructose and achieved 92.3% HMF yield in 40 min reaction time using 10 wt% of catalyst at 70 °C reaction temperature [3].

5. CONCLUSION

Biomass is the most abundant renewable resource that can be converted to energy, chemicals, foods and feedstocks. An excellent strategy for providing a new energy source is the immediate use of the inedible biomass, such as cereal straws, bagasse and even used

paper. Cellulose is the major component of such biomass, which occupies 60–80% of biomass. Utilization of biomass, especially inedible cellulosic biomass, is highly desirable for the construction of sustainable society.

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