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Ubiquitous aluminum alkyls and alkoxides as effective catalysts for glucose to HMF conversion in ionic liquids

Dajiang (DJ) Liu [a,b], Eugene Y.-X. Chen [a,*]

[a] Department of Chemistry, Colorado State University, Fort Collins, CO 80523, USA
[b] Department of Mechanical Engineering, Colorado State University, Fort Collins, CO 80523, USA

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ABSTRACT

Metal halides (chlorides in particular) are employed almost exclusively as Lewis acid catalysts for the homogeneous conversion of glucose (or cellulose) to HMF (5-hydroxymethylfurfural) in ionic liquids (ILs), with $CrCl_2$ being arguably the most effective benchmark catalyst. Reported herein is a discovery that ubiquitous aluminum alkyl or alkoxy compounds are very effective Lewis acid catalysts for the glucose-to-HMF conversion in ILs. Under the current reaction conditions (1-ethyl-3-methylimidazolium chloride [EMIM]Cl, 120 °C, 6 h), simple trialkyl and trialkoxy aluminum species such as $AlEt_3$ and $Al(O^iPr)_3$, which are much cheaper than $CrCl_2$ (by a factor of 5 for $AlEt_3$ or 180 for $Al(O^iPr)_3$), are at least as effective as $CrCl_2$ to catalyze this conversion process. The molecular structure of $[EMIM]^+[ClAlMe(BHT)_2]^-$, formed upon mixing the alkylaryloxy aluminum $MeAl(BHT)_2$ and the IL [EMIM]Cl, has been determined by X-ray diffraction; the structure simulates that of the metallate $[EMIM]^+[CrCl_3]^-$, the proposed active species responsible for the effective glucose to HMF conversion by $CrCl_2$ in [EMIM]Cl. Another significant finding is that a gradual substitution of the chloride ligand on aluminum by the alkyl ligand brings about a drastic enhancement on the HMF yield, from 1.6% by $AlCl_3$ to 7.6% by $MeAlCl_2$ to 17% by Et_2AlCl and to 51% by $AlEt_3$, thus showing approximately an overall 32-fold HMF yield enhancement going from $AlCl_3$ to $AlEt_3$.

1. Introduction

Research directed at developing effective conversion of non-food plant biomass into fuels and/or chemicals has intensified in recent years [1], as this process, once becoming technologically and economically competitive as compared to oil refinery, can provide humanity with a sustainable source of fuels and chemicals. The majority (60–90 wt.%) of plant biomass is the biopolymer carbohydrates (sugars) stored in the form of cellulose and hemicelluloses. The biomass-derived sugars can be converted into fuels and value-added chemicals by liquid-phase catalytic processing [2]. Alternatively, cellulosic materials can be directly converted into the biomass platform chemical 5-hydroxymethylfurfural (HMF) [3], a versatile intermediate for top-value-added chemicals and fuels (e.g., 2,5-dimethylfuran, a biofuel with a 40% higher energy density than ethanol [4]). As environmentally benign alternatives to volatile organic solvents, recyclable ionic liquids (ILs) have attracted rapidly growing interest [5], particularly in the pursuit of renewable energy and chemicals from lignocellulosic biomass [6]. These advances were made possible by the discovery of Rogers and co-workers [7] that showed a class of water-stable and -miscible ILs, 1-alkyl (R)-3-methylimidazolium chloride salts [8], [RMIM]Cl, can solubilize cellulose in appreciable wt.% by disrupting the extensive H-bonding network present in cellulose through H-bonding of the anion of ILs with the hydroxyl groups of cellulose [9]. Excitingly, IL solvents enabled homogenous hydrolysis of cellulose to water-soluble reducing sugars in high to quantitative conversion, either catalyzed by mineral or organic acids [10], or even in the absence of any additional catalyst (i.e., with IL–H_2O mixtures) [11].

Through acid-catalyzed dehydration, fructose can be readily converted to HMF typically in high yields [12]. However, glucose, a more desirable feedstock derived from non-food, cellulosic biomass, has been showed to be resistant to its conversion into HMF, thus achieving typically low yields (∼10%) by a variety of catalyst systems, such as lanthanide halides $LnCl_3$ ($Ln = La^{3+}–Lu^{3+}$) in water or organic solvents [13]; the use of $AlCl_3$ in water or organic solvents assisted by microwave radiation improves the HMF yield [14]. Seminar work of Zhang et al. revealed that glucose can also be converted into HMF in good yields when using $CrCl_2$ as catalyst in ILs such as [EMIM]Cl [15]. Thus, the $CrCl_2$-catalyzed process in [EMIM]Cl at 100 °C for 3 h achieved a HMF yield of 68–70%; the process was proposed to proceed via in situ glucose-to-fructose isomerization catalyzed by the anion $CrCl_3^-$ in the resulting

* Corresponding author at: Department of Chemistry, Colorado State University, Fort Collins, CO 80523 1872, USA. Tel.: +1 970 491 5609; fax: +1 970 491 1801.
E-mail address: eugene.chen@colostate.edu (E.Y.-X. Chen).

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