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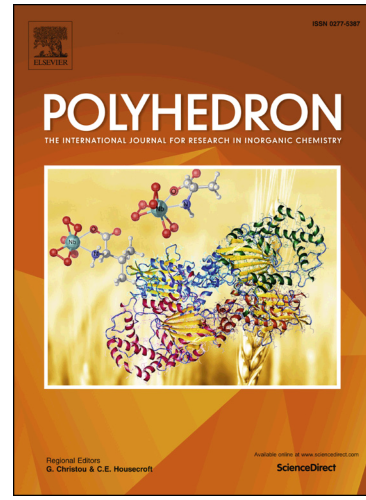

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Effect of ancillary (aminomethyl)phenolate ligand on efficacy of aluminum-catalyzed glucose dehydration to 5-hydroxymethylfurfural

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ABSTRACT

Air-stable dimethylaluminum complexes L^RAlMe_2 that contain (aminomethyl)phenolate (L^R) ligands were prepared in high yield. NMR data and X-ray crystallographic characterization of the molecular structures of several of the complexes confirmed bidentate coordination of the (aminomethyl)phenolate ligand to aluminum. Efficient aluminum catalysts for glucose dehydration to HMF were generated via modification of the (aminomethyl)phenolate ligand. L^RAlMe_2 complexes containing bidentate (aminomethyl)phenolate ligands with an aryl substituent on the amino moiety are efficient catalysts for glucose dehydration to HMF in ionic liquid solvents. In [EMIM]Br and [BMIM]Br, the reaction proceeds at 120 ˚C to very high conversion in 2 hours to produce HMF with 60-63% selectivity and in 58-60% yield. Evidently, L^RAlMe_2 complexes catalyze glucose isomerization to fructose at ≥120 ˚C while the HMF yield depends on the degree of competing HMF loss to humins formation. These results indicate that additional studies of ancillary ligand effects on aluminum-catalyzed glucose dehydration are needed to improve knowledge of structure-function relationships that are key to increasing the efficiency of aluminum catalysts for dehydration of glucose (and ultimately cellulose) to HMF.

1. Introduction

Glucose is the most abundant monosaccharide in cellulosic biomass hence efficient catalytic processes for its conversion into chemicals and biofuels are highly desirable [1-3]. Glucose dehydration is a promising method for synthesis of 5-hydroxymethylfurfural (HMF), an emerging bio-derived platform chemical that potentially could be used to produce a wide variety of high-value chemicals [4, 5]. For example, HMF can be converted by selective oxidation into 2,5-furandicarboxylic acid (FDCA) which is attractive as a substitute for terephthalic acid in plastics production [6, 7]. HMF can also undergo rehydration to produce levulinic acid (LA) which itself is a promising platform chemical that can be used as a feedstock for production of liquid hydrocarbon fuels [8, 9].

Investigations of glucose dehydration [5] using different catalysts (such as organic and inorganic acids, Lewis acids, salts, and zeolites) and solvents (including aqueous, organic, mixed aqueous/organic, and ionic liquids) have established that glucose conversion to HMF with Brønsted acids (such as HCl and H_2SO_4) typically proceeds via direct dehydration of glucose to HMF while with Lewis acid catalysts, the reaction typically proceeds via formation of fructose [6, 10]. However, while mineral acids usually give HMF in low yield and produce other byproducts, moderate-to-high yields of HMF have been reported in ionic liquids and high boiling organic solvents with various Lewis acid metal salts, such as $CrCl_2$ [11-13], $SnCl_4$ [14, 15], and $AlCl_3$ [10, 16-18] as catalysts.

Given the much lower toxicity and cheaper cost of Al in comparison to Cr and Sn, the development of efficient Al catalysts for glucose conversion to HMF is receiving increased attention [10, 16-20]. For example, Abu-Omar and coworkers have reported that $AlCl_3$ exhibits high glucose conversion activity in water/THF biphasic medium to give HMF in 61% yield [16]. Dumensic and coworkers have found that catalytic conversion of glucose with the combination of $AlCl_3$ and a Brønsted acid (such as HCl) in a biphasic water/alkylphenol solvent system gave 62% yield of HMF [10]. Rasrendra et al. used both $AlCl_3$ and $Al(OTf)_3$ in DMSO for glucose conversion to produce HMF in 50% and 60% yield, respectively [21]. Liu and Chen showed that aluminum trialkyls (such as pyrophoric $AlMe_3$ and $AlEt_3$) and trialkoxides (such as $Al(OPr^i)_3$ and $Al(OBu^t)_3$) can give up to 50% HMF yield from glucose conversion in [EMIM]Cl [20]. These studies indicate that aluminum species hold strong promise as Lewis acid catalysts for glucose conversion to HMF. However, the majority of studies used (10-30%) $AlCl_3$ in different solvents, and current knowledge of ancillary ligand effects on the efficiency of glucose conversion to HMF with aluminum Lewis acid catalysts is lacking. Herein, we report a systematic study of the efficacy of easily prepared,