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Short Communication

$InCl_3$-catalyzed conversion of carbohydrates into 5-hydroxymethylfurfural in biphasic system

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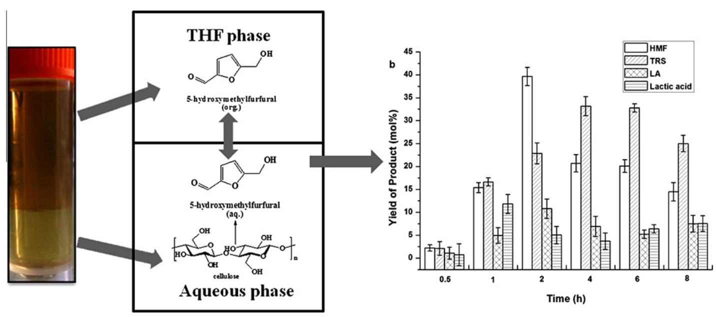
HIGHLIGHTS

- NaCl-H_2O/THF system was developed for conversion of cellulose into HMF.
- NaCl has the benefit of increasing the partitioning ratio ($M_{org.}/M_{aq.}$).
- The biphasic system was useful for different feedstocks.

GRAPHICAL ABSTRACT



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ABSTRACT

$InCl_3$, a water-compatible Lewis acid, was used for the conversion of microcrystalline cellulose to produce 5-hydroxymethylfurfural (HMF) in a H_2O/THF biphasic system. Addition of NaCl increased the HMF yield significantly but suppressed the levulinic acid (LA) formation. The HMF yield of 39.7% was obtained in 2 h at 200 °C in the NaCl-H_2O/THF catalytic system catalyzed by $InCl_3$. The catalytic system also showed effectiveness to convert other carbohydrates to HMF, including glucose, fructose, sucrose, starch, which demonstrated great potential towards different feedstocks.

1. Introduction

The limited reservoir of fossil resources, the increasing demands for energy, and the growing emissions of CO_2 have stimulated research into the production of chemicals and fuels from biomass (Huber et al., 2006). The conversion of lignocellulosic biomass to fuels and chemicals requires effective use of the C5 and C6 sugars in hemicelluloses and cellulose. The C6 sugars, glucose and fructose, as well as starch and cellulose, have been used to produce useful platform chemicals, such as 5-hydroxymethylfurfural (HMF) and levulinic acid (LA) (Román-Leshkov et al., 2007; Dutta et al., 2012).

Recent progresses have been achieved in HMF production from the cheap and abundant glucose in ionic liquids, organic solvents, water, and biphasic systems (He et al., 2013; Zhou et al., 2013; Qu et al., 2012; Choudhary et al., 2013). During the above

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processes, the efficient downstream separation of HMF from high-boiling organic solvents or ionic liquids and the recycling of the reaction media pose challenges to the commercialization of these catalytic systems. Consequently, water appears to be a better choice for HMF production. Additionally, water-compatible Lewis acid indium trichloride ($InCl_3$), as an easy-handling and eco-friendly catalyst that imparts high region-selectivity and chemo-selectivity in various chemical transformations, has been proposed as a promising catalyst for the conversion of biomass into chemicals. In our previous works, it has been demonstrated to be an efficient catalyst for the glucose (aldose) to fructose (ketose) isomerization reaction in water (Shen et al., 2014). Meanwhile, water-contained biphasic systems are proved to be more cost-effective. In recent years, a series of organic solvents such as methylisobutylketone (MIBK), 1-methyl-2-pyrrolidinone (NMP), and 2-butanol are reported to be efficient as extraction solvent in biphasic system, making the HMF production from monosaccharides feasible for commercial use (Pagàn-Torres et al., 2012).

Compared with dehydration of monosaccharides to HMF, direct conversion of cellulose into HMF is more attractive and challenging. Direct transformation of cellulose into HMF usually involves three steps: (1) hydrolysis of polymeric cellulose into monosaccharide, (2) isomerization from glucose (aldose) to fructose (ketose), allowing five-membered ring formation, and (3) dehydration of fructose (ketose) to generate HMF. Binder et al. obtained a high HMF yield of 54 mol% form cellulose in the DMA-LiCl solvent with $CrCl_3$ and HCl as co-catalyst (Binder and Raines, 2009). Yu et al. also obtained a high HMF yield of 62 mol% from cellulose in the ionic liquid 1-butyl-3methylimidazolium chloride with $CrCl_3$/LiCl as catalyst (Yu et al., 2011) Li et al. performed a one-step reaction sequence in which cellulose was converted to HMF catalyzed by $InCl_3$ in ionic liquid (Li et al., 2013). However, the HMF yield obtained from cellulose in the biphasic system is still low compared to that obtained in the ionic liquid and polar aprotic solvents.

In this work we developed a cost-effective method for the production of HMF with high yield from carbohydrates using $InCl_3$ as catalyst. In order to avoid the rehydration of HMF to LA and remove HMF from the reactant sugar and acidic catalyst, tetrahydrofuran (THF) was used to continuously extract HMF from the aqueous phase. In addition, NaCl, which is among the most effective and cheapest inorganic salts, was also investigated to increase the partition ratio between THF and water.

2. Methods

2.1. Materials

Glucose (99%), fructose (99%), sucrose (99%), soluble starch (AR), micro-crystalline cellulose (DP = 215–240, 90 μm) (extra pure graded), THF and NaCl were purchased from Sinopharm Chemical Reagent Co., Ltd (Beijing, China) and used without further purification. $InCl_3$ (99%) was purchased from Tianjin Jinke Fine Chemical Research Institute (Tianjin, China). HMF (AR, 98%), levulinic acid (AR, 98%), and lactic acid (AR, 90%) were supplied by Acros Organics.

2.2. Conversion of cellulose into HMF

Conversion of cellulose was carried out in a 50 ml stainless steel reactor with a Teflon inner. In a typical experiment for single phase, cellulose (0.41 g, 2.5 mmol based on glucose units), $InCl_3$ (0.015 g, 50 mM), NaCl (3.5 g), and nanopure water (10 ml) were loaded into the reactor; in a typical experiment for biphasic system, cellulose (0.41 g, 2.5 mmol), $InCl_3$ (0.015 g, 50 mM), NaCl (3.5 g), nanopure water (10 ml), and THF (30 ml) were used. Then, the reaction was heated to 200 °C for 2 h. The liquid products were analyzed by gas chromatography–mass spectrometry (GC–MS), ultraviolet–visible spectrophotometer (UV), and high-performance liquid chromatography (HPLC) instruments.

2.3. Total reducing sugar analysis

Reducing sugars (i.e., glucose, cellobiose, and higher soluble oligodextrins) indicated the rate of cellulose hydrolysis. Total reducing sugar (TRS) was measured by DNS method using D-glucose as a standard on an ultraviolet–visible spectrophotometer at 540 nm. The mass of TRS M_{TRS} and the yield of TRS Y_{TRS} were calculated as follows: M_{TRS} (mg) = TRS concentration (mg/ml) × 25 (ml) × (V_1/1). Y_{TRS} (%) = $M_{TRS} \times 0.9/M_{cellulose} \times 100\%$. In which, V_1 is the volume of the sample, and 0.9 is the ratio of glucose unit of cellulose and molecular weight of glucose.

Table 1
Comparison of different catalytic system for HMF production derived from cellulose catalyzed by $InCl_3$.[a]

Entry	Solvent system	Conv. (mol%)	Product yield (mol%)[b]			
			TRS	HMF	LA	Lactic acid
1	H_2O	40.1 ± 0.9	11.8 ± 2.0	1.1 ± 0.8	12.2 ± 1.3	7.0 ± 1.5
2	H_2O-NaCl	43.4 ± 1.3	11.3 ± 1.5	3.4 ± 1.0	0.3 ± 1.7	10.9 ± 2.3
3	H_2O/THF	66.7 ± 1.7	21.9 ± 2.1	22.4 ± 3.1	7.0 ± 1.8	6.7 ± 2.1
4	NaCl-H_2O/THF	87.6 ± 2.2	22.9 ± 1.4	39.7 ± 1.5	10.8 ± 0.8	5.0 ± 2.3

[a] Reaction conditions: cellulose, 2.5 mmol; $InCl_3$, 50 mM; NaCl, 3.5 g; H_2O, 10 ml; THF, 30 ml; 200 °C; 2 h.
[b] TRS, total reducing sugar; HMF, 5-hydroxylmethyfurfal; LA, levulinic acid.

Table 2
The conversion comparison of different raw materials catalyzed by $InCl_3$ in NaCl-H_2O/THF biphasic system.[a]

Entry	Starting material	Conv. (mol%)	Product yield (mol%)[b]			
			TRS	HMF	LA	Lactic acid
1	Glucose	99.0 ± 1.3	15.4 ± 1.5	50.9 ± 0.9	18.3 ± 1.1	8.8 ± 0.7
2	Fructose	99.1 ± 2.0	19.0 ± 1.6	54.3 ± 0.8	16.6 ± 2.2	10.9 ± 1.4
3	Sucrose	98.3 ± 0.7	15.3 ± 1.3	51.7 ± 0.9	16.5 ± 2.0	10.8 ± 1.9
4	Starch	90.6 ± 2.3	20.7 ± 1.2	46.0 ± 1.4	2.5 ± 2.5	8.1 ± 1.5
5	Cellulose	87.6 ± 0.8	22.9 ± 1.1	39.7 ± 0.7	10.8 ± 2.6	5.0 ± 1.8

[a] Reaction conditions: starting material, 2.5 mmol; $InCl_3$, 50 mM; NaCl, 3.5 g; H_2O, 10 ml; THF, 30 ml; 200 °C; 2 h.
[b] TRS, total reducing sugar; HMF, 5-hydroxylmethyfurfal; LA, levulinic acid.