



Elucidating the role of cobalt phthalocyanine in the dehydration of carbohydrates in ionic liquids



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ABSTRACT

The cobalt(II) phthalocyanine efficiently converts glucose and cellulose into 5-hydroxymethylfurfural in [EMIm]Cl ionic liquid. From various throughout screening of metal salts, metallophthalocyanines and ionic liquids, the combination of cobalt phthalocyanine with [EMIm]Cl ionic liquid gave the best results. Co(II)Pc interacts with glucose in [EMIm]Cl ionic liquid and in situ generates the Co(I)Pc and Co(III)Pc which are confirmed from UV–visible analysis. Co(III)Pc reacts with glucose and generates five membered ring chelate complex, which subsequently isomerizes to fructose. In the reaction fructose easily dehydrates to HMF. A single-pot EMF and DFF are produced by etherification and aerobic oxidation reaction of glucose, respectively. The catalyst is easily separated from the reaction by simple filtration and recycled upto 3–5 times without the significant loss of its catalytic activity.

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1. Introduction

In recent years, the increasing consumption of natural petroleum feedstock leads us to find an alternative source. All the forest plants, woods and herbaceous energy crops contain good amount of cellulose, hemicelluloses and lignin as major constituent [1]. The presence of extensive hydrogen-bonded networks and van der Waals interactions in sugar polymers, make it difficult to hydrolyze. Therefore the replacement of petroleum feedstocks with biomass requires the development of efficient and cost-effective procedure to convert carbohydrates to a variety of useful chemical compounds [2–4].

5-Hydroxymethylfurfural (HMF) is an important organic compound which serves as a versatile intermediate between biomass-based carbohydrate chemistry [5,6] and petroleum-based industrial organic chemistry [7–9]. HMF and its derivatives potentially replace voluminously consumed petroleum-based building blocks, which are currently used to make plastics and fine chemicals. HMF is easily converted into smaller building blocks [10] like 2,5-diformylfuran (DFF) [11], 2,5-furandicarboxylic acid [12], polyethyleneterephthalate [10], 5-(ethoxymethyl)furfural (EMF)

[10], polybutyleneterephthalate [10], 2,5-dihydroxymethylfuran, [11] etc. Previously starting with glucose and fructose, many catalytic systems for the synthesis of HMF are reported in organic solvents [13], water [14], ionic liquids [15] and in microwave conditions [16]. These procedures require either protonic acid [17] or metal salt as a Lewis acid catalyst [18]. This acid catalyzed dehydration of carbohydrates leads to various side-products like levulinic acid [19], formic acid [10], furfural [20], humic acid, etc. and separation of HMF is tough from these side products. However starting with cellulose and other feedstocks, very few literature reports are available and these procedures require higher temperature with higher pressure [10].

In this paper, we have developed a simple and convenient strategy for the dehydration of cellulose and glucose to HMF by using the Lewis acidic character of cobalt phthalocyanine. Recently we have carried out various organic transformations like oxidation, reduction and dechlorination of various organic moieties [21] by using cobalt phthalocyanines as a catalyst. Thus metallophthalocyanines easily replace metal catalysts from organic transformations and provide better substitute. The unsubstituted metallophthalocyanines are insoluble in common organic solvents but they easily interact with ionic liquids. Ionic liquids have been used as a green solvent to replace the conventional organic solvents due to their unusual properties particularly low vapor pressure and flammability, highly concentrated ionic atmosphere, thermal stability, fast ion transport and ease of recyclability [22]. The combination of ionic liquids and metal salts are effective catalysts [23] for the hydrolysis

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of cellulose, therefore we have chosen the ionic liquids as a green reaction media.

Herein, we report the use of highly concentrated carbohydrate melts for the selective conversion of glucose and cellulose into HMF. Different reaction conditions for heterogeneous catalysis were investigated. The in situ generated Co(III)Pc shows better Lewis acidic character for the isomerization of glucose. In this catalytic system, the highly desirable biofuel EMF and DFF were synthesized in one pot reaction from glucose in better yield and purity.

2. Experimental

The ^1H NMR spectrum was measured in CDCl_3 at ambient temperature on a JEOL 400 MHz instrument. The chemical shifts are given in ppm related to tetramethylsilane (TMS) as internal standard. HPLC was performed in (C-18 reverse phase column); water:MeOH = 80:20, flow rate = 0.6 mL min^{-1} , monitored at 284 nm. The external standard curve method (HPLC) was employed for the quantification of the product. The standards (HMF, EMF, DFF, levulinic acid and formic acid) were obtained from Sigma–Aldrich, India. UV–vis spectra were recorded on a Perkin-Elmer Lambda 35 UV-Vis. spectrophotometer and absorption maxima have been expressed in nm. IR spectra were recorded on a Perkin-Elmer Spectrum 2000 infrared spectrophotometer. Glucose and cellulose were obtained from Spectrochem Pvt. Ltd. and was used as such as received. All the solvents are of HPLC grade. All the reactions were carried out under argon atmosphere until it is mentioned. Metallophthalocyanines (**1a–1e**) and ionic liquids (**2a–2c**) were synthesized by following the procedures [24] reported by us.

2.1. General procedure for the conversion of glucose to HMF in neutral ionic liquids (**2a**) catalyzed by cobalt phthalocyanine (**1a**)

In a typical reaction, glucose (200 mg, 1.11 mmol) was heated to 100°C in [EMIm]Cl (324 mg, 2.22 mmol) and after 5 min catalyst **1a** (42 mg, 0.0556 mmol) was added to reaction mixture at the same temperature. The reaction was monitored by TLC. After completion of reaction, ethyl acetate (10 mL) was added to the reaction, organic layer was separated and dried over sodium sulfate. The product was analyzed by HPLC and other spectroscopic technique.

^1H NMR (400 MHz, CDCl_3): 3.16 (brs, 1H, OH), 4.7 (s, 2H, CH_2), 6.52 (d, 1H, furan H), 7.23 (d, 1H, furan H), 9.56 (s, 1H, CHO); ^{13}C NMR (75 MHz, CDCl_3): 57.02 (CH_2), 109.85 (furan CH), 123.54 (furan CH), 151.87 (furan C), 161.08 (furan C), 177.75 (CHO); HR Q-TOF MS, m/z : 127.08 (M+1) (calcd for $\text{C}_6\text{H}_4\text{O}_3$ 126.02).

2.2. General procedure for the hydrolysis of cellulose to HMF

In a typical reaction, cellulose (500 mg) was heated to 140°C in [EMIm]Cl (5 g) to form a homogeneous mixture and after 30 min catalyst **1a** (200 mg) was added to the reaction mixture at the same temperature. The reaction was monitored by TLC. After completion of reaction (4.5 h), the reaction mixture was extracted with ethyl acetate ($5 \times 10\text{ mL}$) and dried over sodium sulfate. Products were analyzed by HPLC. HMF was obtained in 65% yield. Ionic liquid **2a** was separated from cellulose by addition of water to reaction mixture.

2.3. Synthesis of DFF

2.3.1. Synthesis of DFF from HMF

For typical experiments, in a 50 mL round bottom flask, HMF (100 mg, 0.7936 mol), 5 wt% of the cobalt phthalocyanine **1a** (30 mg) and IL **2a** (232 mg) were heated with continuous stirring at 80°C for 1 h under oxygen atmosphere. Upon completion of reaction, the reaction mixture was cooled to room temperature. Ethyl

acetate (10 mL) was added to the reaction and organic layer was separated and dried over sodium sulfate (anhydrous). The product was analyzed by HPLC and other spectroscopic techniques.

^1H NMR (400 MHz, CDCl_3): 7.4 (s, 2H, furan H), 9.8 (s, 2H, CHO); ^{13}C NMR (75 MHz, CDCl_3): 120.4 (s, CH), 154.8 (s, qC), 179.7 (s, CHO); HR Q-TOF MS, m/z : 125.09 (M+1) (calcd for $\text{C}_6\text{H}_4\text{O}_3$ 124.02).

2.3.2. One-pot synthesis of DFF from glucose

In a typical reaction, glucose (200 mg, 1.11 mmol) was heated to 100°C in [EMIm]Cl (324 mg, 2.22 mmol) and after 5 min catalyst **1a** (42 mg, 0.0556 mmol) was added to reaction mixture at the same temperature. The reaction was stirred under nitrogen atmosphere until the completion of the reaction. After completion of reaction, it was cooled down and oxygen was provided to the reaction by balloon and it was further heated to 80°C . The reaction was monitored by TLC. The product was isolated in the same way as described above.

2.4. Synthesis of EMF

2.4.1. Synthesis of EMF from HMF

For typical experiments, in a 50 mL round bottom flask, HMF (100 mg, 0.7936 mol), 5 wt% of the cobalt phthalocyanine **1a** (30 mg) and IL **2a** (232 mg) in 5 mL ethanol were refluxed with continuous stirring at 90°C for 2 h using a long condenser and chilled water so that ethanol vapor can be condensed back to the liquid phase. Upon completion of reaction, the reaction mixture was cooled to room temperature and ethanol was evaporated under vacuum. To the oily residue, 10 mL distilled water was added and the product was extracted with ethyl acetate ($3 \times 10\text{ mL}$). The organic layer was dried on sodium sulfate and evaporated under vacuum to give the desired product. The product was characterized by ^1H NMR spectroscopy.

^1H NMR (400 MHz, CDCl_3): 9.59 (s, 1H), 7.19 (d, $J = 2.8\text{ Hz}$, 1H), 6.50 (d, $J = 2.8\text{ Hz}$, 1H), 4.53 (s, 2H), 3.69 (q, 2H), 1.20 (t, 3H).

2.4.2. One-pot synthesis of EMF from glucose

One-pot production of EMF from glucose was carried out in ethanol by oil-bath heating. A 100 mL round-bottom flask was charged with glucose (200 mg), 5 wt% of cobalt phthalocyanine **1a** (42 mg) and IL **2a** (325 mg) catalysts in 10 mL ethanol and was refluxed with continuous stirring at 90°C for 3 h. After completion of the reaction, the oily liquid product was isolated in the same way as described above. The ^1H NMR spectrum of the isolated product revealed the presence of both EMF and EL in the reaction mixture.

2.5. Analysis

The product yields, conversion, and selectivity were determined as follows:

$$\text{Product yield, \%} = \frac{\text{weight of products}}{\text{weight of cellulose put into reactor}} \times 100$$

$$\text{Cellulose conversion, \%} = \frac{\text{moles of reacted cellulose}}{\text{moles of initial cellulose}} \times 100$$

$$\text{Product selectivity, \%} = \frac{\text{moles of product obtained}}{\text{moles of reacted cellulose}} \times 100$$

3. Results and discussion

For the dehydration of carbohydrates, metallophthalocyanines (Fig. 1) are chosen as a solid catalyst and ionic liquids (Fig. 2) as a green reaction media. The required metallophthalocyanines are synthesized from phthalonitriles by following up the procedure

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