



Short communication

# The effect of manganese(II) chloride as a co-catalyst on cellobiose hydrolysis in dilute aqueous sulfuric acid and acidic ionic liquid mediums



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## ABSTRACT

The effects of adding  $\text{MnCl}_2$  as a co-catalyst on cellobiose hydrolysis in 0.016 M aqueous  $\text{H}_2\text{SO}_4$  and 0.032 M 1-(1-propylsulfonic)-3-methylimidazolium chloride acidic ionic liquid mediums were studied at 60–90 °C by measuring the glucose yields. The addition of  $\text{MnCl}_2$  produced enhancements in glucose yields in both aqueous acid mediums. The yield enhancements are highest at 60 °C and gradually decrease at higher temperatures, suggesting that a weak interaction of  $\text{MnCl}_2$  with cellobiose causes the co-catalytic effect. FT-IR studies in the solid-state suggest that  $\text{MnCl}_2$  interacts with hydroxyl groups of cellobiose without causing significant changes in the pyranose ring conformations.

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## 1. Introduction

Cellulose is the most abundant renewable organic polymer on earth. The efficient depolymerization of this biopolymer to its monomer glucose is an essential and challenging step in the use of the lignocellulosic biomass in cellulosic ethanol production via sugar fermentation route [1]. Acid catalyzed cellulose depolymerization or hydrolysis using dilute aqueous sulfuric acid at high temperature and pressure was the traditional method used in early cellulosic-ethanol plants in the 1940s, which was mostly replaced by enzyme process due to low sugar yields. However, in recent years numerous research groups have studied the possibility of improving the classical aqueous sulfuric acid catalyzed cellulose hydrolysis due to costs associated with enzymatic methods, which requires an energy consuming pre-treatment before the biochemical hydrolysis using expensive cellulase enzymes [2]. Some of the new directions taken in enhancing the acid catalysis process are: use of organic acids such as aryl/alkyl sulfonic acids, malic acid, in place of sulfuric acid [3,4], mechanical activation such as ball milling [5] as well as incorporation of co-catalysts to acid catalyst system [6–8]. The addition of metal ions as a co-catalyst for enhancing the effect of an acid is a logical choice as one can expect the complexation or interaction of metal ions with hydroxyl groups of the carbohydrate may facilitate the action of the Brønsted acid [6–8]. In addition, metal ions or their complexes are the traditional catalysts in many industrial processes. However the use of metals as catalysts or co-catalysts in cellulose depolymerization or pre-treatments is a relatively new development.

The transition metal salts have been tested as co-catalysts in a handful of examples [9–11]. For instance small amount of ferrous sulfate has been shown to increase the glucose yield from 74% to 78% during the  $\text{SO}_2\text{-H}_2\text{SO}_3$  pretreatment of spruce wood chips [11]. Additionally Zhao et al. have examined the effects of transition metal ions  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$  as co-catalysts in the acid hydrolysis of corn stover under microwave irradiation conditions [9], where the co-catalysts enhance the total reducing sugar (TRS) yields in the order  $\text{Fe}^{3+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+}$ . Furthermore, a 3.0% concentration of ferrous sulfate as a co-catalyst produced the highest reducing sugar yield of 35.10% [9]. The pretreatment and saccharification with metal ion itself acting as a Lewis acid without the use of a Brønsted acid is also known. In this example sugarcane bagasse was pretreated with different metal chlorides:  $\text{CrCl}_3$ ,  $\text{FeCl}_3$ ,  $\text{FeCl}_2$ ,  $\text{ZnCl}_2$  and  $\text{AlCl}_3$  before the enzymatic hydrolysis and  $\text{FeCl}_3$  pretreatment produced the highest sugar yield [12]. In addition, halide salts of alkali and alkali earth metals are also known to improve the hydrolysis of cellobiose under microwave heating conditions [13].

There are several reports on isolation and X-ray crystallographic structure determination of monosaccharide–metal complexes, this includes  $\text{Ca}^{2+}$  complexes of D-fructose [14], D-galactose [15], lactose [16], D-mannose [17], trehalose [18], D-xylose [19], D-arabinose [20], D-ribose [21] and  $\text{LaCl}_3$ -ribose [22]. Though, the only structural study of a metal complex of the cellulose model compound D-cellobiose is the X-ray structure of  $\alpha$ -cellobiose  $\cdot$   $2\text{NaI} \cdot 2\text{H}_2\text{O}$  complex [23]. Furthermore, only a very few studies have attempted to address the mechanisms of metal promoted depolymerization and dissolutions of cellulose [24–26]. In a recent example, Zhang et al. have studied the role of  $\text{Li}^+$  and  $\text{Cl}^-$  ions in the dissolution of cellulose in dimethyl acetamide–LiCl system by NMR methods [26]. Where they found that the hydroxyl

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protons of cellulose form strong hydrogen bonds with the  $\text{Cl}^-$  during which the intermolecular hydrogen bonding networks of cellulose are broken with simultaneous splitting of the  $\text{Li}^+$  and  $\text{Cl}^-$  ion pairs [26].

Since 2009 we have been exploring the use of alkyl/aryl sulfonic acids [3], sulfonic acid group functionalized acidic ionic liquids [27,28] as catalysts for the saccharification of cellulose and lignocellulosic biomass for cellulosic ethanol process as well as other biofuel applications. We first reported the use of imidazolium type –  $\text{SO}_3\text{H}$  functionalized Brønsted acidic ionic liquid (BAIL) 1-(1-propylsulfonic)-3-methylimidazolium chloride as an acid catalyst for the depolymerization of cellulose [27]. In the follow-up work we found that these acidic ionic liquids can be used as homogeneous catalysts in aqueous phase as well [28]. Recently we have studied the effect of a series of metal ions:  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{La}^{3+}$  as their chloride salts on 1-(1-propylsulfonic)-3-methylimidazolium chloride acidic ionic liquid catalyzed hydrolysis of cellulose in water at 140–170 °C. During this work,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Co}^{2+}$  as co-catalysts produced significant enhancements in total reducing sugar (TRS) yields, with  $\text{Mn}^{2+}$  showing the highest activity.  $\text{Mn}^{2+}$  as co-catalyst produced 91.8, and 91.9% TRS yields, whereas samples without  $\text{Mn}^{2+}$  gave 28.0 and 28.7% yields at 160 and 170 °C respectively. As a continuation of this effort and as an attempt to elucidate the mechanism of co-catalytic effect of manganese(II) chloride on cellulose hydrolysis, we have studied the effect of  $\text{MnCl}_2$  on the hydrolysis of cellulose model compound cellobiose in dilute sulfuric acid and in aqueous acidic ionic liquid mediums of similar acid strengths as shown in Fig. 1.

## 2. Experimental

### 2.1. Materials and instrumentation

D-Cellobiose (99.9%), 1-methylimidazole, 1,3-propanesultone, sulfuric acid (99%) and  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (99.9%) were purchased from Aldrich Chemical Co. Brønsted acidic ionic liquid catalyst was prepared by condensation of 1-methylimidazole with 1,3-propanesultone and acidification of the resulting salt with conc. HCl as shown in Fig. 2, according to the literature procedure [29,30]. Cellobiose hydrolysis experiments were carried out by heating solutions in glass vials, in a Cole-Parmer Stable Temp digital utility water bath (model: WU-14576-00) with temperature stability of  $\pm 0.1$  °C. The glucose produced in the hydrolysis was measured using glucose oxidase–peroxidase enzymatic assay [31] using a Thermo Scientific GENESYS 10S UV/Vis spectrophotometer and 1.00 cm quartz cells. FT-IR spectra were recorded on a Thermo Nicolet IR 200 using KBr pellets at  $1.0\text{ cm}^{-1}$  resolution.

### 2.2. General experimental procedures for the hydrolysis of cellobiose in aqueous sulfuric acid and 1-(1-propylsulfonic)-3-methylimidazolium chloride solutions with and without $\text{MnCl}_2$ co-catalyst

A mixture of cellobiose (15.0 mg, 0.044 mmol) and  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (1.8 mg, 0.009 mmol) in 5.00 mL of 0.016 M aqueous sulfuric acid was prepared in a 20 mL glass vial with a screw cap. The vial was firmly closed and heated in a thermostated water bath maintained at the desired temperature for 2.0–10.0 h. Next the vial was removed from the hot water bath and immediately cooled in an ice-bath to quench the reaction. The contents were neutralized by drop wise addition of

0.5 M aq. NaOH and the glucose formed was immediately measured using glucose oxidase/peroxidase enzymatic assay as described in Section 2.3. A similar experiment without the metal salt was used as the reference. The average glucose percent yields produced in a series of experiments in duplicate using aqueous sulfuric acid mediums at temperatures 60, 70, 80 and 90 °C, and reaction times: 2.0, 4.0, 6.0, 8.0, 10.0 h with  $\text{MnCl}_2$  as co-catalysts, as well as without co-catalysts are shown in plots a–d in Fig. 3.

A similar series of experiments using 0.032 M aqueous 1-(1-propylsulfonic)-3-methylimidazolium chloride medium in place of aqueous sulfuric acid was also carried out under identical conditions and their glucose percent yields at 60, 70, 80 and 90 °C are also shown in plots a–d in Fig. 3.

### 2.3. Glucose assay

A 0.20 mL sample of the neutralized cellobiose hydrolyzate was transferred to a glass vial and 1.80 mL of distilled water was added. Then 2.00 mL of the glucose oxidase/peroxidase reagent was added, mixed thoroughly and immediately incubated in a water bath maintained at 37 °C for 30 min. The reaction was quenched after 30 min incubation period by adding 2.00 mL of 6 M HCl to give a pink solution. The reagent blank was prepared by mixing 2.00 mL of deionized water and 2.00 mL of assay reagent, and was treated similarly. Then the absorbance was immediately measured at 540 nm against the reagent blank and glucose concentration in the solution was calculated by employing a standard curve prepared using glucose.

### 2.4. FT-IR experiments

A mixture of cellobiose (34.2 mg, 0.1 mmol) and  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (19.8 mg, 0.1 mmol) were prepared and ground together for 2.0 min. Using a pestle and mortar. Then a 5 mg portion of the mixture was thoroughly mixed with 100 mg of dry KBr and was used in making the KBr pellet for recording the spectrum.

A mixture of cellobiose (34.2 mg, 0.1 mmol),  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (19.8 mg, 0.1 mmol) and 1-(1-propylsulfonic)-3-methylimidazolium chloride (24.1 mg, 0.1 mmol) was also prepared and FT-IR spectrum was recorded under similar conditions. A FT-IR spectrum of pure cellobiose recorded under the same conditions was used as the reference spectrum and these spectra are shown in Supplementary data.

## 3. Results and discussion

### 3.1. Cellobiose hydrolysis with $\text{MnCl}_2$ co-catalyst

The ionic liquid 1-(1-alkylsulfonic)-3-methylimidazolium chloride and metal chloride  $\text{MnCl}_2$  as the co-catalyst were chosen for the cellobiose hydrolysis experiments based on our earlier studies. In our earlier experiments on screening metal salts as co-catalysts for cellulose hydrolysis, the highest catalytic effect enhancement was observed in samples where manganese(II) chloride was used as the co-catalyst [32]. For example the cellulose samples hydrolyzed using BAIL with  $\text{Mn}^{2+}$  as co-catalyst produced TRS yields of 59.1, 78.4, 91.8, and 91.9% at 140, 150, 160, and 170 °C respectively; whereas cellulose hydrolyzed without  $\text{Mn}^{2+}$  produced TRS yields of 9.8, 16.5, 28.0, and 28.7% at the same

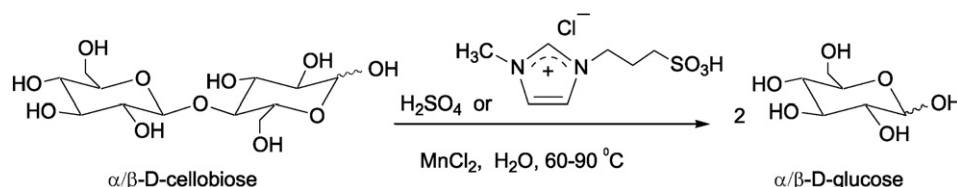


Fig. 1. Hydrolysis of cellobiose in dilute aqueous sulfuric acid and in acidic ionic liquid mediums using  $\text{MnCl}_2$  as a co-catalyst.

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