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## Hydrolysis of Cellulose in 1-allyl-3-methylimidazolium

## chloride Catalyzed by Methyltrioxorhenium

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**Abstract**: Methyltrioxorhenium (MTO) has been applied as catalyst to promote cellulose hydrolysis by using the ionic liquid 1-allyl-3-methylimidazolium chloride ([Amim]Cl) as solvent. When using 7 mol% of MTO, 70  $\mu$ L of water, ca. 0.6 mmol of microcrystalline cellulose and 2.0 g of [Amim]Cl under microwave irradiation for 30 min at 150 °C, 51.2 % of total reducing sugar (TRS) and 24.7 % of glucose yield can be obtained. The nucleophilic attack of electron-rich O atom of  $\beta$ -1,4-glycosidic bond to electron-poor Re atom of MTO, leading to the broken of  $\beta$ -1,4-glycosidic bond, is assumed to be crucial for cellulose degradation.

Keywords: Microcrystalline Cellulose, Hydrolysis, Methyltrioxorhenium, Ionic liquid

#### **1** Introduction

Due to the diminishing of fossil resource, the utilization of alternative energy resources is becoming particularly important [1]. Lignocellulosic biomass is one of the most abundant renewable resources [2], which is a promising feedstock for the production of biofuels and value-added chemicals. Hydrolysis of cellulose to sugars under mild conditions is a practical transformation route since sugars can be further converted into some chemicals, such as alcohols (ethanol, butanol), hydrogen, methane or 5-hydroxymethylfurfural (5-HMF) [3-5]. Cellulose is a kind of highly crystalline polymer that composed of D-anhydroglucopyranose units joined together via  $\beta$ -1,4-glycosidic bonds [6]. Owing to the tight hydrogen-bonding networks and van der Waals, cellulose is very stable and insoluble in water and most common organic solvents, which makes it difficult to hydrolysis [7].

Ionic liquids (ILs), which are considered as environmental benign solvents or reagents, have attached considerable attention in many transformation processes [8]. Rogers *et al.* found that ILs can be used as efficient solvent to dissolve cellulose [9], which have been received huge attention by researchers [10]. Subsequently, various ILs including imidazolium salt have been found effective for cellulose dissolution. In recent years, chloride anion based ILs have also been appeared to be the most effective solvents for dissolving cellulose, such as 1-allyl-3-methylimidazolium chloride ([Amim]Cl), 1-ethyl-3-methylimidazolium chloride ([Emim]Cl), and 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) [7,11]. It has been found that Cl<sup>-</sup>

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could coordinate with the hydroxyl group of cellulose, which would disrupt the hydrogen bonding system of cellulose and lead to the dissolution of cellulose [9]. Lignocellulose can be treated by acid hydrolysis (mineral acids and metal chlorides) and enzymatic hydrolysis (cellulases) [12-18]. Bogel-Łukasik et al. have extensively studied the enzymatic hydrolysis of carbohydrate-rich and cellulose-rich feedstocks obtained from wheat straw after pre-treatment with 1-ethyl-3-methylimidazolium acetate ([Emim][CH<sub>3</sub>COO]), whereas a total sugar release could be achieved [15]. Mikkola et al. also utilized various ILs as pre-treatment solvents for different lignocelluloses, and developed an enzymatic hydrolysis and ethanol fermentation transformation, in coupled method for lignocellulose which excellent glucan-to-glucose conversion could be obtained after the enzymatic hydrolysis of IL-treated substrates [16]. Despite enzymatic hydrolysis in ILs proved to be efficient, the major disadvantages for enzymatic hydrolysis in industry are the high cost and low activity of enzyme [19]. In the process of acid hydrolysis, the equipment of serious corrosion and the environmental pollution by the large amounts of acid waste water also cannot be avoided. Moreover, owing to the poor solubility of cellulose in acid solution, acid hydrolysis has to be performed under high temperature and sometimes even high pressure [20, 21].

MTO is a kind of organometallic catalyst, which was firstly synthesized by Beattie and Jones in 1979 [22]. Subsequently, Herrmann, Espenson, and Adam found that MTO was an extremely versatile catalyst for a variety of organic reactions, such as epoxidations, dihydroxylations, and carbon-carbon double bond cleavage of various unsaturated compounds [23-26]. Although MTO has been studied for decades, it has not yet been examined as catalyst for cellulose hydrolysis. Given our continuous interests in both cellulose transformation and MTO chemistry, we attempted to explore the reactivity of MTO-catalyzed hydrolysis of cellulose. In this work, MTO is for the first time reported as a catalyst for the hydrolysis of cellulose under mild conditions.

### **2** Experimental

#### 2.1. Materials and methods

Microcrystalline cellulose (MCC, average particle size of 50  $\mu$ m), 3,5-dinitrosalicylicacid (DNS, CP,  $\geq$  98 %), phenol (AR,  $\geq$  99.5 %), potassium sodium tartrate (AR,  $\geq$  99 %), were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). [Amim]Cl (CP,  $\geq$  99 %) was purchased from Lanzhou Institute of Chemical Physics (Lanzhou, China). MTO was prepared according to the published procedures [26].

#### 2.2. Typical procedure for the hydrolysis of cellulose

MCC and [Amim]Cl were dried thoroughly under vacuum at 90 °C and 80 °C respectively prior to cellulose hydrolysis. In a typical procedure, MCC (0.1 g, 0.6 mmol) and [Amim]Cl (2.0 g) were mixed and then heated at 100 °C with stirring for 10 min to form a homogeneous and transparent solution. A certain amount of MTO and H<sub>2</sub>O were then added, and the mixture was treated with microwave irradiation at a given temperature and time. After the reaction was completed, the mixture was

quenched immediately with cold deionized water and then filtered. The filtrate was diluted to 100 mL for analysis.

#### 2.3. TRS analysis

DNS method is used for TRS determination. 3.0 mL of DNS reagent and 1.0 mL of diluted solution were added into a test tube, heated at 100 °C for 30 min, then diluted with deionized water to 20 mL. The absorbance was measured by a sp-752pc ultraviolet-visible (UV) spectrophotometer at 540 nm. The concentration of TRS was determined on the basis of the standard curve of glucose.

#### 2.4. High performance liquid chromatograph (HPLC) analysis

Agilent 1100 series HPLC, which was equipped with an ultraviolet detector and a Bio-Rad Aminex HPX-87H column, was used to analyze the sample solution. The column temperature was 65 °C, and a 5 mmol·L<sup>-1</sup> sulfuric acid aqueous solution was used as the mobile phase at a flow rate of 0.6 mL/min. The yield of products was calculated according to calibration curves.

### **3** Results and discussion

In this work, cellulose was hydrolyzed in [Amim]Cl using MTO as catalyst. It can be observed that a white mixture was formed when 0.1 g of cellulose was mixed in [Amim]Cl, and the mixture became a homogeneous and transparent solution after heating at 100 °C with stirring for 10 min (see Fig. S1 of Supporting Information). The solution became dark black when catalyzed by 7 mol% of MTO under microwave irradiation at 160 °C for 30 min (Fig. S1). Such a color change may due to the decomposition of cellulose or sugars to chars or humins. In all examined samples, glucose, 5-HMF and a small amounts of furfural (< 0.6 %), acetic acid (< 2.5 %), formic acid (< 2 %), acetyl acid (< 1 %), and some other non-identified products could be detected.

#### 3.1. Hydrolysis of cellulose

It has been reported that the addition of certain water can promote cellulose hydrolysis [27]. To carefully determine the effect of MTO and water on cellulose hydrolysis, the reactions were carried out under the conditions of without water and catalyst, with water, with catalyst, and with both water and catalyst at different temperatures (see Fig. S2 of Supporting Information). The results indicated that reaction temperature had a significant influence on the hydrolysis of cellulose. Both TRS and glucose yields increased gradually with the increasing of reaction temperature, and the maximum values were obtained at 150 °C. However, the yields began to decrease when the temperature was above 150 °C. It might because that, with the temperature increasing, the viscosity of reaction system decreased and at the same time mass transfer rate of reaction system increased, which could make a complete catalyst contact with cellulose. However, when the temperature was above 150 °C, glucose and other monosaccharide could also convert to 5-HMF or other byproducts which would lead to the decrease of TRS and glucose yields. When the reaction was performed without catalyst and water, only 6 % of glucose and 18 % of TRS yields can be obtained at 150 °C. The yields were slightly increasing after adding water and MTO to the system, and the corresponding data increased up to 51.2 % and 24.7 % respectively after applying 70  $\mu$ L of water and 7 mol % of catalyst. The data clearly indicated that both MTO and water could promote cellulose hydrolysis, and the best hydrolysis temperature was 150 °C.

In order to get the insight of the influence of reaction time on the hydrolysis reaction, TRS and glucose yields were compared under the conditions of different time at 150 °C. The results showed that the favorable hydrolysis time was 30 min under microwave irradiation, which the TRS yield of 51.2 % and glucose yield of 24.7 % could be obtained (Fig. 1). With the increasing of reaction time, the TRS and glucose yields increased gradually, and then reached the maximum in 30 min. However when the reaction time was more than 30 min, the yields of TRS and glucose reduced accordingly. They were respectively down to 26 % and 12 % in 60 min of microwave irradiation at 150 °C. These results could be due to the side reactions (the decomposition of sugars to 5-HMF, humins or other byproducts), which finally resulted in the decrease of TRS and glucose yields.



Fig. 1. Time-dependent TRS and glucose yields.

The influence of catalyst and water amount on TRS and glucose yields were carefully investigated and the results were summarized in Table 1. In general, both TRS and glucose yields increased gradually with the increasing of catalyst amount with the range of 1 - 7 mol% (Table 1, entries 2 - 5), and then decreased when the amount of MTO was more than 7 mol% (Table 1, entries 6 - 7). It might due to the further transformation of glucose to byproducts with the excessive catalyst. TRS and glucose yields increased rapidly with the amount of water increasing from 0 to 70  $\mu$ L (Table 1, entries 5, and 8 - 11), while the yields of TRS and glucose decreased when the amount of water was above 70  $\mu$ L (Table 1, entries 12 - 13). The decline of the yields was due to the decrease of the solubility of cellulose in solvent with excessive water. It could be also observed that, if more than 70  $\mu$ L water was applied, the cellulose solution would result in the precipitation of cellulose from IL solution.

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Entry	Catalyst	Water	TRS <sup>b</sup>	Glucose <sup>c</sup>	5-HMF <sup>c</sup>
	(mol%)	(µL)	(%)	(%)	(%)
1	0	70	24.7	5.7	0.4
2	1	70	34.1	11.2	2.3
3	3	70	38.6	15.8	5.3
4	5	70	45.5	18.7	6.9
5	7	70	51.2	24.7	7.2
6	9	70	33.0	10.7	6.9
7	15	70	27.8	8.8	2.7
8	7	0	37.1	15.9	4.0
9	7	10	41.6	17.5	5.1
10	7	30	44.3	19.8	4.9
11	7	50	47.4	21.8	5.6
12	7	90	37.7	14.2	4.8
13	7	110	34.9	10.6	3.6

#### Table 1

The effects of catalyst and water amount on cellulose hydrolysis <sup>a</sup>

<sup>a</sup>The reaction was carried out under microwave heating using MCC (0.6 mmol, 0.1 g), [Amim]Cl (2.0 g) as solvent and MTO as catalyst for 30 min at 150 °C;

<sup>b</sup>TRS was detected by DNS method;

<sup>c</sup>The yield of glucose and 5-HMF were calculated according to HPLC analysis.

Accordingly, the highest TRS and glucose yields obtained were 51.2% and 24.7% respectively under the condition of 7 mol% of MTO, 70  $\mu$ L of water, ca. 0.6 mmol of microcrystalline cellulose and 2.0 g of [Amim]Cl under microwave irradiation for 30 min at 150 °C. Comparing to the reported Brønsteded acidic ILs such as 1-butyl-3-methylimidazolium hydrogen sulfate [Bmim]HSO<sub>4</sub> [27, 28] or 1-(1-propylsulfonic)-3-methylimidazolium chloride ([PSmim]Cl) [29] promoted cellulose hydrolysis processes, the examined system showed lower TRS and glucose yields. Nevertheless, the corrosion problem originated from acidic ions such as HSO<sub>4</sub> in IL can be avoided in MTO/[Amim]Cl cellulose degradation system.

### 3.2. Mechanism Considerations

Based on literature precedents [5, 30, 31], the mechanism for hydrolysis of cellulose catalyzed by MTO in [Amim]Cl is proposed (Fig. 2). First, MCC is dissolved in [Amim]Cl and form a homogeneous and transparent solution, which would lead to a dissociation of super molecular structure of cellulose in [Amim]Cl [32]. Since the oxygen atom of Re=O in MTO bears the lone pair electrons, the oxygen atom of Re=O might be able to interact with the hydroxyl group of cellulose via hydrogen bonding, thus MTO is able to reach the surface of cellulose molecules. The subsequent nucleophilic attack of electron-rich O atom of  $\beta$ -1,4-glycosidic bond to electron-poor Re atom of MTO leads to the broken of  $\beta$ -1,4-glycosidic bond. In the meantime, water is inserted into  $\beta$ -1,4-glycosidic bond, resulting in the formation of a MTO coordinated glucose (or other cellobiose and polysaccharide) intermediates [30, 31]. The further dissociation of MTO from the product leads to the formation of

glucose and the recovered MTO. On the other side, similar to  $CrCl_3$  or other metal salts [5] catalyzed glucose transformations, the MTO coordinated glucose may also promote the isomerization of glucose to fructose. Thus, subsequent dehydration of fructose could result in the formation of the 5-HMF product.



Fig.2 . Proposed mechanism for cellulose hydrolysis with MTO and water.

#### **4** Conclusions

For the first time, MTO was used as catalyst to promote the hydrolysis of cellulose in ionic liquid [Amim]Cl. The effect of reaction temperature and time, catalyst and water amount on cellulose hydrolysis was discussed in details. The results indicated that MTO can promote the hydrolysis of cellulose. Moreover, water proved to be also effective. 51.2 % of TRS yield and 24.7 % of glucose yield could be obtained under the condition of 7 mol% of MTO as catalyst, 70  $\mu$ L of water, ca. 0.6 mmol of MCC and 2.0 g of [Amim]Cl as solvent under microwave irradiation at 150 °C for 30 min. The reaction mechanism for cellulose hydrolysis to sugar and 5-HMF catalyzed by MTO is proposed, whereas the coordination of electron-rich O atom of  $\beta$ -1,4-glycosidic bond, is assumed to be crucial for the degradation cellulose. Moreover, MTO could also promote the isomerization of 5-HMF.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.201X.XX.XXX.

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# **Graphical Abstract**

Graphical Abstract (Figure):



Graphical Abstract (Text): Hydrolysis of cellulose catalyzed by methyltrioxorhenium under microwave irradiation in 1-allyl-3-methylimidazolium chloride

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## Highlights

•Methyltrioxorhenium (MTO) is for the first time applied as catalyst to promote the hydrolysis of

cellulose in ionic liquid [Amim]Cl.

- •MTO displays good catalytic performance for cellulose hydrolysis.
- •The nucleophilic attack of electron-rich O atom of  $\beta$ -1,4-glycosidic bond to electron-poor Re atom of MTO leads to the broken of  $\beta$ -1,4-glycosidic bond.