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β-1,4-glycosidic bond, is assumed to be crucial for cellulose degradation.

Short communication

Hydrolysis of cellulose in 1-allyl-3-methylimidazolium chloride catalyzed by methyltrioxorhenium



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ABSTRACT

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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 is composed of Danhydroglucopyranose units joined together via β -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 hydrolyze [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 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 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⁻ could coordinate with the hydroxyl group of cellulose, which would disrupt the hydrogen bonding system of cellulose and

Corresponding author. E-mail address: ShuliangZang@163.com (S. Zang). 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 celluloserich feedstocks obtained from wheat straw after pre-treatment with 1-ethyl-3-methylimidazolium acetate ([Emim][CH₃COO]), 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 coupled method for lignocellulose transformation, in which excellent glucan-toglucose conversion could be obtained after the enzymatic hydrolysis of IL-treated substrates [16]. Despite that 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].

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 µL 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 β -1,4-glycosidic bond to electron-poor Re atom of MTO, leading to the broken of

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 a 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.



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2. Experimental

2.1. Materials and methods

Microcrystalline cellulose (MCC, average particle size of 50 μ m), 3,5-dinitrosalicylic acid (DNS, CP, \geq 98%), phenol (AR, \geq 99.5%), and 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 H₂O was 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⁻¹ 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 be due to the decomposition of cellulose or sugars to chars or humins. In all examined samples, glucose, 5-HMF and 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.



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

However, the yields began to decrease when the temperature was above 150 °C. It might be 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 µL 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, in 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

Table 1	
The effects of catalyst and water amount of	on cellulose hydrolysis ^a

Entry	Catalyst (mol%)	Water (µL)	TRS ^b (%)	Glucose ^c (%)	5-HMF ^c (%)
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

 $^{\rm a}\,$ 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.

^b TRS was detected by DNS method.

^c The yields of glucose and 5-HMF were calculated according to HPLC analysis.

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