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Kinetic studies on chromium-catalyzed conversion of glucose into 5-hydroxymethylfurfural in alkylimidazolium chloride ionic liquid

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HIGHLIGHTS

- The reaction is second order in glucose with an activation energy of 134.9 kJ mol^{-1}.
- The order of the reaction in chromium is first.
- The observed rate constant decreases as initial glucose concentration increases.
- A kinetic model was developed to describe glucose conversion and 5-hydroxymethylfurfural formation.

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ABSTRACT

5-Hydroxymethylfurfural (HMF) is a promising green platform chemical derived from biomass. Kinetic studies were performed on chromium chloride-catalyzed conversion of glucose into HMF in alkylimidazolium chloride ionic liquids. The main by-products are disaccharides, fructose, glyceraldehyde, formic acid, and humins. The formation of HMF is strongly affected by reaction temperature and initial glucose concentration. The reaction is second order in glucose, with an activation energy of 134.9 kJ mol^{-1}. The order in chromium is first, indicating that the rate-determining isomerization reaction is catalyzed by a mononuclear chromium species. The observed glucose conversion rate constant decreases as initial glucose concentration increases, suggesting that the catalytic activity of the chloride anion is significantly restrained by the hydrogen bonding with hydroxyl groups. A simplified kinetic model is developed to describe the behaviors of glucose conversion and HMF formation. This model is in good agreement with the experimental results.

1. Introduction

Concerns about energy crisis and global warming have led to the exploration of bio-fuel and fine chemical production from carbon–neutral renewable biomass [1,2]. The five-membered ring compound 5-hydroxymethylfurfural (HMF) is one of the top platform chemicals derived from biomass, which can be used to synthesise a variety of useful acids, aldehydes, alcohols, amines currently obtained from petroleum, and the remarkable fuel 2,5-dimethylfuran [3,4]. Despite high expectations on the industrial use of HMF, its commercial manufacturing process remains a great challenge, mainly because of high production costs [5].

Currently, utilization of widely available raw materials such as sucrose, starch and cellulose for HMF production has drawn much attention, among which cellulose is highly attractive because its low price and does not pose a threat for global food supply [5,6]. All the sugar mentioned above contain glucose monomer, thus the development of simple and effective process to transform glucose into HMF would be of great significance. However, conversion of glucose in traditional solvents, such as water, organic solvents, organic/water mixed solvents and sub/super critical water, often affords low HMF yield because it tends to form stable pyranose structure which has a low enolization rate [7–14]. Zhao et al. [15] first developed a chromium (II) chloride/ionic liquid (IL) system that converted glucose with a good HMF yield. Since then, numerous related studies have been conducted, including further exploiting the chromium system and finding new catalysts for the direct conversion of glucose into HMF [16–21]. The vast majority of studies involving the successful transformation of glucose

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Nomenclature

[glu]	concentration of glucose (mol/L)
$[glu]_0$	initial concentration of glucose (mol/L)
[fruc]	concentration of fructose (mol/L)
[HMF]	concentration of HMF (mol/L)
k_G	total reaction rate constant of glucose decomposition $((mol/L)^{-1}\ s^{-1})$
k_1	reaction rate constant of fructose decomposition into HMF $((mol/L)^{-1}\ s^{-1})$
k_2	reaction rate constant of fructose decomposition into humins $((mol/L)^{-1}\ s^{-1})$

into HMF mainly concern IL-mediated catalysis by chromium chloride, which results in HMF yields between 60% and 90% [5].

Owing to its highly efficient HMF preparation from glucose, the reaction mechanism of glucose conversion in ILs has attracted much interest. Isotopic labeling studies indicated that the key aldose-to-ketose conversion in glucose dehydration occured via a 1, 2-hydride shift, which was also found to be catalyzed by Lewis acid such as Sn and Al other than chromium catalyst [15,22–25]. The "1,2-hydride shift" was usually believed to be catalyzed by mononuclear active center. However, recent density functional theory (DFT) calculations indicated that a dimeric complex of Cr was favored, which would lower the H shift energy barrier [26,27]. A detailed mechanism of glucose dehydration catalyzed by bimolecular Cr complex is shown in Scheme 1. Apart from the controversy regarding chromium species, the reaction order in glucose in IL also needs to be reinvestigated. Glucose decomposition is generally described as a first-order process in aqueous solution [9,28–31]. Nevertheless, recent investigations on catalytic glucose conversion in dimethyl sulfoxide (DMSO) by metal salts provided a new case, where the order in glucose was shown to be second [32].

Kinetic studies have played a key role in the mechanistic elucidation of many chemical reactions. However, far little work has been done on the glucose conversion in ILs. Herein, 1-Allyl-3-methylimidazolium chloride ([Amim]Cl), 1-ethyl-3-methylimidazolium chloride ([Emim]Cl), and 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) were chosen as solvents and $CrCl_3{\cdot}6H_2O$ was used as the catalyst. This work aims to present kinetic evidence for the glucose conversion mechanism and propose a kinetic model for both glucose conversion and HMF formation.

2. Materials and methods

2.1. Materials

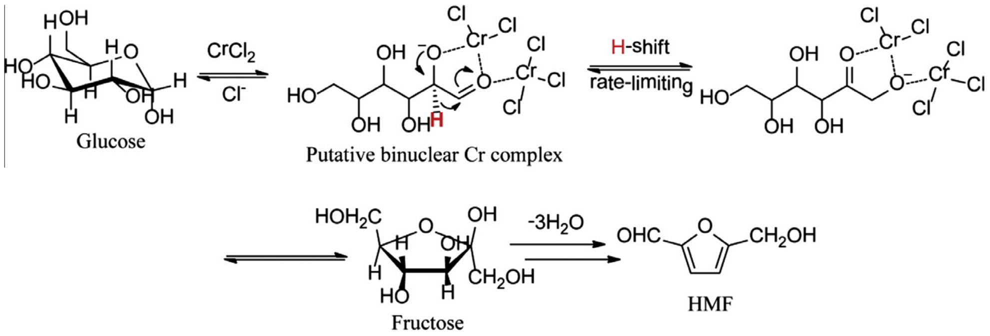
[Amim]Cl was synthesised according to the method described by Zhang et al. [33]. 1-Methylimidazole (99%, Kaile Chemical Reagent Co., Ltd., China) was distilled from CaH_2 prior to use. Allyl chloride (99%, Xinbao Chemical Co., Ltd., China) was distilled prior to use. [Emim]Cl (99%) and [Bmim]Cl (99%) were purchased from Shanghai Cheng Jie Chemical Co., Ltd., China. Glucose anhydrous (analytical grade, Sinopharm Chemical Reagent Co., Ltd.) was dried to constant in vacuo at 353 K prior to use. $CrCl_3{\cdot}6H_2O$ was provided by Tianjin Shentai Chemical Reagent Co., Ltd. All other chemicals were commercially available in China and used as received.

2.2. Synthesis of HMF from sugars

Experiments were carried out at a given temperature (353–393 K) in a three-necked flask (100 mL) with a mechanical stirrer (350 rpm). No increase in reaction rate was found upon increasing the stirring rate to 450 rpm. The initial glucose concentration varied from 5 to 20 wt.% (relative to total mass) and the catalyst loading ranged from 2 to 12 mol% corresponding to moles of glucose. ILs (25 mL) and the predetermined amount of glucose were placed in the flask. The mixture was then stirred and heated to the reaction temperature (±1 K) within 20 min. After the mixture turned into a transparent solution, $CrCl_3{\cdot}6H_2O$ was added and the start time t_0 for the kinetic measurements was taken at the time of catalyst addition. The progress of the reaction was monitored by periodically taking small (about 0.1 g) aliquots from the reactor. The corresponding mixture was then diluted with de-ionized water in a 10 mL volumetric flask, filtered through 0.22 μm nylon filters, and analyzed using high-performance liquid chromatography (HPLC). The reproducibility of the experimental results ranged from 97% to 98%.

2.3. Analysis

The composition of the liquid phase was determined using an Agilent 1200 series HPLC system equipped with an Agilent 1200 series refractive index detector and a Bio-rad Aminex HPX-87H ion exclusive column (300 mm × 7.8 mm). The mobile phase applied was a 5 mM H_2SO_4 aqueous solution at a flow rate of 0.6 mL/min. The column was operated at 333 K and the volume for each injection was 20 μL. Previous studies analyzing glucose decomposition products provided us with a starting point for determining unknowns [34–36]. Peak identification was established by a comparison of sample peak retention time with that of a standard solution of the pure compound. The product



Scheme 1. Proposed mechanism for glucose dehydration catalyzed by chromous chloride [22].