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Production of levulinic acid from glucosamine using zirconium oxychloride

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ABSTRACT

In this study, we evaluated zirconium oxychloride ($ZrOCl_2$), an eco-friendly Lewis acid as a catalyst for conversion of glucosamine (a monomer of chitosan obtained from shell-crustacean food waste) into levulinic acid (LA). In a $ZrOCl_2$-catalyzed hydrothermal reaction, 21.29 mol% of LA was obtained using optimized conditions with 50 g/L glucosamine and 15 mol% $ZrOCl_2$, at 200 °C for 20 min. Our results demonstrate the potential of glucosamine as a recyclable feedstock and $ZrOCl_2$ as an eco-friendly catalyst for platform chemical synthesis.

Introduction

Decrease in fossil fuel reserves occurs due to irreversible environmental contamination and global climate change; therefore, renewable and sustainable energy and material resources have been developed to replace fossil resources [1–3]. Bioresources such as sugar, starch, lignocellulose, and macro-algae are attractive alternatives to fossil resources. They can replace carbon skeletons in fossil resources and produce various bio-based products via thermochemical and bio-refinery processes [2–4].

Among various biomass-derived platform chemicals, 5-hydroxymethylfurfural (5-HMF) is a renewable and versatile intermediate, and has been used in the production of various biofuels and materials [2–7]. Levulinic acid (LA), a versatile green chemical, is a highly valued bio-based chemical [2–6]. Currently, LA is commercially produced from fossil resources using the petrochemical process; however, difficulties such as rising cost of fossil resources and environmental problems have hampered its production [5]. To overcome these problems, various thermochemical processes have been introduced to produce LA from bioresources such as sugar, starch, lignocellulose, algae, and chitin/chitosan [5–16]. Owing to the two reactive groups (carbonyl and carboxy groups) of LA, it can be converted into various valuable chemicals including pharmaceuticals, fuels, solvents, and polymers [5,6,11].

In this study, we evaluated glucosamine as biomass source for the production of chemical intermediates such as 5-HMF and LA. Chitin/chitosan is one of the most abundant nitrogen-containing biopolymers (carbohydrates) [8–13,16,17]. Glucosamine is a monomer of chitosan. In addition, it has a chemical structure similar to glucose. In general, chitin/chitosan is commercially obtained from food waste of shell-crustaceans in the fish industry [18]. Chitosan and glucosamine have been widely used in industries including pharmaceuticals, medical treatment, biomaterials, food/feed, agricultural products, and wastewater treatment [8,11,17]. Recently, chitin/chitosan has been proposed for use in producing biofuels and chemicals such as 5-HMF and LA [8–13,16].

In recent years, several homogeneous Lewis acidic metal chloride catalysts have been used to produce 5-HMF and LA from sugars, starch, and lignocellulose [5,6,9,10,12,19–22]. In addition, synthesis of 5-HMF derivatives via catalytic oxidation of biomass-derived 5-HMF using a modified zirconium catalyst was reported [7]. Although the potential of zirconium oxychloride ($ZrOCl_2$) as a catalyst is known in several reactions [19–22], there is limited information on using $ZrOCl_2$ to produce 5-HMF and LA from carbohydrates. $ZrOCl_2$ is an attractive and interesting catalyst in organic reactions because of its low toxicity, ease of handling, reusability, moisture stability, availability, abundance, and low cost [23]. In addition, it is an eco-friendly Lewis acid (LD_{50} (oral rat) = 2950 mg/kg) [23,24]. Recently, some studies have reported production of 5-HMF from fructose, glucose, cellulose, maple wood, corn stover, and sugarcane bagasse using $ZrOCl_2$ [19–22]. However, no studies have reported conversion of glucosamine into 5-HMF or LA using $ZrOCl_2$ as a catalyst.

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Therefore, in this study, we investigated the potential of $ZrOCl_2$-catalyzed hydrothermal conversion of glucosamine for production of platform chemicals such as 5-HMF and LA. To optimize reaction conditions, effects of reaction variables including reaction temperature, $ZrOCl_2$ concentration, glucosamine concentration, and reaction time were investigated. In addition, efficiency of $ZrOCl_2$-catalyzed hydrothermal conversion was evaluated using the combined severity factor (CSF).

Materials and methods

Materials

Glucosamine HCl was purchased from Sigma–Aldrich Co., Ltd. (USA). The $ZrOCl_2 \cdot 8H_2O$ (Junsei Chemical Co., Ltd., Japan) used was of reagent grade, and LA, 5-HMF, and all other chemicals were of analytical grade.

Experimental procedure

For batch experiments, specific amounts of glucosamine (substrate) and $ZrOCl_2$ (catalyst) were placed in a 2 mL glass vial, and the mixture was vigorously vortexed to dissolve and mix the substrate and catalyst. After the glass vial was sealed, it was inserted into a stainless steel reactor for hydrothermal reaction. The reaction was started when the reactor set temperature was attained in the oil bath, and the preheating time required was approximately 5 min. Upon completion of the reaction, the reactor was quickly cooled to room temperature by dipping in tap water. The product solution was recovered via centrifugation at 17,000 rpm for 10 min and subsequently filtered using a 0.2 μm syringe filter for HPLC analysis [11].

$ZrOCl_2$-catalyzed hydrothermal conversion of glucosamine

Reaction variables in the $ZrOCl_2$-catalyzed conversion of glucosamine were optimized for 5-HMF and LA production; these included reaction temperature, catalyst concentration, biomass concentration, and reaction time. Effect of reaction temperature (140–210 °C) on the conversion of glucosamine into 5-HMF and LA was investigated using 50 g/L glucosamine and 10 mol% $ZrOCl_2$ for 10–60 min. Effect of catalyst ($ZrOCl_2$) concentration (5–50 mol %) was investigated using 50 g/L glucosamine at 200 °C for 10–30 min. Effect of biomass (glucosamine) concentration (25–100 g/L) was investigated using 15 mol% $ZrOCl_2$ at 200 °C for 10–30 min. Finally, effect of reaction time (0–60 min) was investigated at 200 °C using 50 g/L glucosamine and 15 mol% $ZrOCl_2$. All experiments were conducted using two or more repetitions, and data were represented as mean ± SD.

Effect of reaction severity

To evaluate reaction severity, the combined severity factor CSF was used. CSF may be represented as $CSF = \log\left[t\ \exp(T - T_{ref})/14.75\right] - pH$, where, $T(t)$ is the reaction temperature (°C), T_{ref} is the reference reaction temperature (i.e., 100), t is the reaction time (min), and 14.75 is the fitted value of the arbitrary constant. The pH of the solution was measured at room temperature prior to reaction [13,14,25].

Analysis

Concentrations of 5-HMF and LA were measured using an HPLC system (Agilent 1100; Agilent Technologies Inc., USA) with an Aminex-87H column (Bio-Rad, USA) and refractive index detector. HPLC operating conditions were 65 °C oven temperature, 5 mM sulfuric acid as mobile phase, and 0.6 mL/min flow rate [11,14,15].

Calculation of conversion yield

Conversion yield of 5-HMF and LA from glucosamine was calculated using the following equation: Yield (mol%) = mole concentration of product (M)/mole concentration of initial glucosamine (M) × 100. Results were expressed as mean ± SD.

Results and discussion

$ZrOCl_2$-catalyzed hydrothermal reaction of glucosamine

Glucosamine is a monomer of chitin/chitosan, which is a biopolymer derived from exoskeletons of crustaceans and the second most abundant biopolymer on earth [8,11,18]. $ZrOCl_2$ is an attractive and eco-friendly Lewis acid [23]. Furthermore, it is an interesting catalyst in several organic reactions [23]. In this study, we investigated $ZrOCl_2$-catalyzed hydrothermal conversion of glucosamine into 5-HMF and LA. Effects of reaction variables such as reaction temperature, catalyst concentration, biomass

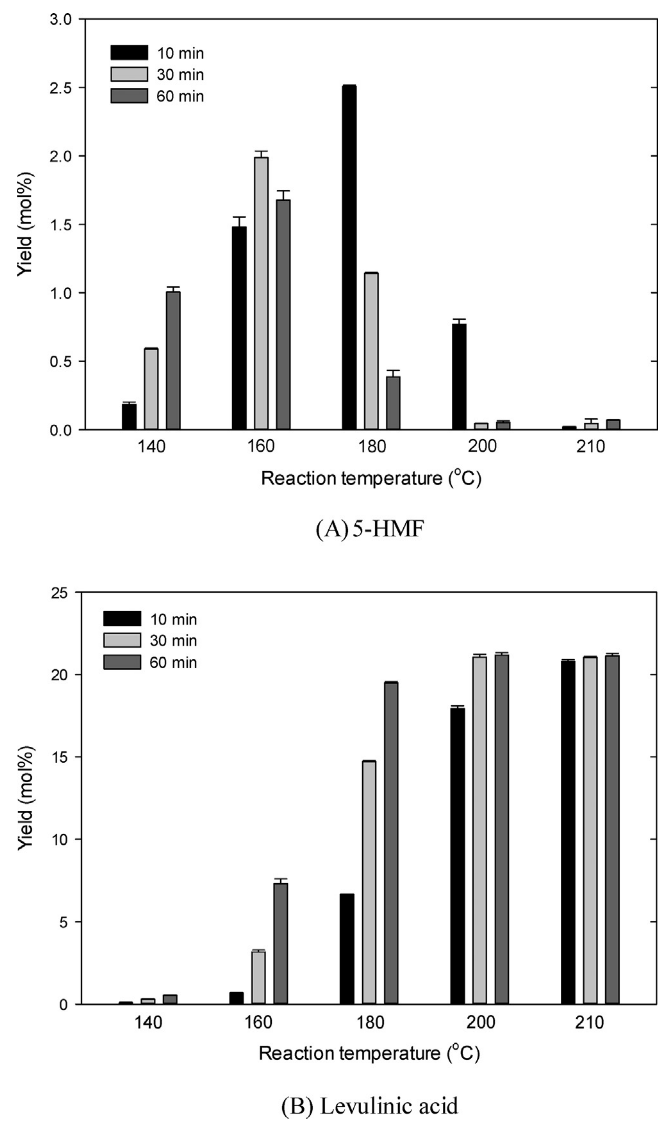

Fig. 1. Effect of reaction temperature on 5-hydroxymethylfurfural and levulinic acid production from glucosamine via $ZrOCl_2$-catalyzed hydrothermal conversion.

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