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Catalysis performance comparison of a Brønsted acid H_2SO_4 and a Lewis acid $Al_2(SO_4)_3$ in methyl levulinate production from biomass carbohydrates

Q1 Xueli Chen, Yuxuan Zhang, Tao Hou, Lujia Han, Weihua Xiao*

College of Engineering, China Agricultural University, Beijing 100083, China

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ABSTRACT

An experimental investigation was conducted to understand the roles of the Brønsted acid H_2SO_4 and Lewis acid $Al_2(SO_4)_3$ in methyl levulinate (ML) production from biomass carbohydrates, including glucose, fructose and cellulose. The product distributions with different catalysts revealed that the Lewis acid was responsible for the isomerization of methyl glucoside (MG), producing a significant amount of the subsequent product 5-methoxymethylfurfural (MMF), while the Brønsted acid facilitated the production of ML from MMF. $Al_2(SO_4)_3$ was efficient for monosaccharide conversion but not for cellulose. Using ball-milled cellulose with $Al_2(SO_4)_3$ resulted in a desired ML yield within a reasonable reaction time. The significant catalysis performances of two types of acids will guide the design of efficient catalytic processes for the selective conversion of biomass into levulinate esters.

1. Introduction

Due to the gradual depletion of fossil resources, efforts to utilize abundant and renewable biomass for the production of liquid fuels and high-quality chemicals have grown [1,2]. The alcoholysis of carbohydrates with an acidic catalyst is a promising method for the conversion of biomass to new platform chemicals, such as alkyl glucoside [3,4], 5-alkoxymethylfurfural [5,6] and alkyl levulinate [7–9], and this method has attracted increasing attention in recent years. As one of the most important target chemicals obtained from biomass resources, alkyl levulinate has been utilized in numerous applications either in medicines, solvents and organic chemistry [10] or as an additive in biodiesel [11]. Furthermore, alkyl levulinate can be widely used in the flavoring and fragrance industries [8].

Many studies have focused on converting carbohydrates into alkyl levulinate in alcohol media using various acidic catalysts, including mineral acids (particularly sulfuric acid) [12–14], metal salts [15] and solid acids [16]. Among these catalysts, the Brønsted acid H_2SO_4 has been widely used as a cheap and active catalyst in the production of levulinates [8,17]. Recently, significant attention has been paid to several metal salts possessing both Brønsted and Lewis acidity, wherein the Lewis acid center that coordinates with oxygen atoms and stabilizes the activated complex formed during the reaction leads to an overall lowering of the activation barrier [18–22]. Zhou et al. [21] discovered that $Al_2(SO_4)_3$ was uniquely effective for the conversion of glucose through its dual Lewis acidity and Brønsted acidity, obtaining a 64% yield of methyl levulinate (ML) at 160 °C over 150 min.

Tominaga et al. investigated the catalytic effect of the Brønsted/Lewis acid ratio (*p*-toluenesulfonic acid (PTSA)) for converting cellulose in methanol, concluding that the highest ML yield (70%) was achieved in a system with a 5/1 ratio of Brønsted/Lewis acid, which showed a higher yield than the single Lewis (52%) or single Brønsted acid (20%) catalyst under identical reaction conditions [23]. Although Tominaga et al. explored the influence of the Brønsted/Lewis acid ratio on the ML yield; limited insight into the product selectivity at the different acid sites in the carbohydrate alcoholysis was provided. Therefore, understanding the functions of the Brønsted and Lewis acid sites on the conversion of intermediates, including methyl glucoside (MG) and 5-methoxymethylfurfural (MMF), to ML is significantly important. Additionally, learning the detailed catalytic effects of the Brønsted and Lewis acid sites on these intermediates will be useful to design efficient catalysts to obtain higher ML yields from biomass.

In this study, we investigate the roles of two typical catalysts (the Brønsted acid H_2SO_4 and the Lewis acid $Al_2(SO_4)_3$) in the alcoholysis reaction and the detailed reaction pathways. The alcoholysis of various carbohydrates, including glucose, fructose and cellulose, is conducted to understand the influences of the Brønsted and Lewis acid sites on different substrates in methanol. Cellulose

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* Corresponding author.
E-mail address: xwhddd@163.com (W. Xiao).

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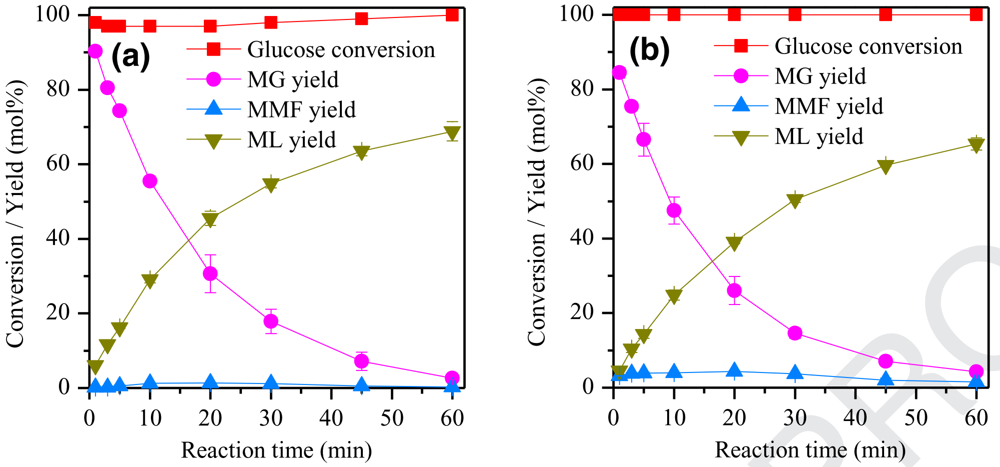

Fig. 1. Effect of the type of catalyst on the glucose conversion and product distribution. Reaction conditions: (a) H_2SO_4 catalyst: 2 g of glucose, 0.35 g of H_2SO_4, 12.6 mL of methanol, and 160 °C; (b) $Al_2(SO_4)_3$ catalyst: 0.4 g of glucose, 0.25 g of $Al_2(SO_4)_3$, 15 mL of methanol, and 160 °C.

pretreated by ball milling is also used as a substrate to gain higher product yield.

2. Experimental

2.1. Chemicals

Glucose (99% purity), fructose (99% purity) and microcrystalline cellulose (particle size: 50 µm) as well as ML, levoglucosenone (LGO), MG and MMF with high purities were obtained from Sigma Aldrich (St. Louis, MO, USA). Other reagents and chemicals were all of analytical grade from the Beijing Chemical Plant (Haidian district, Beijing, China) and used without further purification or treatment.

2.2. Cellulose pretreatment and characterization

2.2.1. Preparation of ball-milled cellulose

Ball-milled cellulose was produced using a CJM-SY-B ultrafine vibration ball mill (Qinhuangdao Taiji Ring Nano Products Co., Ltd., Hebei, China) at room temperature. Microcrystalline cellulose and ZrO_2 balls (6–10 mm in diameter) were mixed in a volume ratio of 1:2 for 1 h, and the instrument temperature was controlled below 30 °C.

2.2.2. X-ray diffraction analysis (XRD)

The crystallinity of cellulose before and after ball-milling pretreatment was evaluated using XD3 X-ray diffractometer (Beijing Purkinje General Instrument Ltd., China) with a Cu-*Kα* radiation source at 40 kV and 30 mA. The scanning scope is $2\theta = 5–40°$ at a rate of 2°/min in 0.2° increments. The crystallinity index (CrI) was calculated based on the method proposed by Segal et al. [24]. The measurements were performed in duplicate.

$$\mathrm{CrI}(\%) = [(I_{002} - I_{\mathrm{am}})/I_{002}] \times 100\%$$

where I_{002} is the maximum intensity of the (002) peak, I_{am} is intensity at approximately $2\theta = 18°$.

2.2.3. Reducing-end determination

The molar concentration of the reducing-end of cellulose samples was measured by the modified BCA method previously described [25]. The measurements were carried out in triplicate.

2.3. Reaction procedure

The experiments were performed in a Milestone microwave lab station (Milestone Co., Italy). The carbohydrate, methanol and a given amount of acid catalyst were added into a 100-mL Teflon reaction vessel and mixed with a magnetic stirrer. The reaction sample temperature was maintained at 160 °C for a pre-set duration from 1 to 60 min with varying microwave power irradiation and a 2450 MHz microwave frequency. After the reaction was completed, the vessel was quenched in an ice water bath to terminate the reaction. All experiments were performed in duplicate, and average values were calculated.

2.4. Analytical approach

The ML and LGO in reaction mixtures were quantitatively analyzed by gas chromatography (GC) (Shimadzu GC-2014C) equipped with a DB-5 capillary column with dimensions of 30 m × 250 mm × 0.25 µm and a flame ionization detector (FID). Nitrogen was used as the carrier gas, and the following temperature program was applied: starting temperature of 50 °C for 2 min, heating rate of 6 °C /min to 180 °C for 3 min, heating rate of 10 °C/min to a final temperature 250 °C, and maintaining this final temperature for 8 min. The quantitative analysis for glucose, fructose, MG and MMF was performed using high-performance liquid chromatography (HPLC) (Hitachi L-7200 with an L-2490 refractive index detector, Hitachi Ltd., Tokyo, Japan) with a BP-800 H^+carbohydrate column (Benson Polymeric, Reno, NV, USA). The mobile phase was 5 mM H_2SO_4 (sonicated and deaerated) in ultrapure water (Milli-Q, Millipore, Billerica, MA) with a flow rate of 0.6 mL/min, and the column temperature was maintained at 55 °C. Conversion of glucose/fructose and the molar product yield were calculated using the following equations:

$$\text{Glucose/fructose conversion} = \frac{\text{moles of glucose/fructose converted}}{\text{moles of starting glucose/fructose}} \times 100\%$$

$$\text{Product yield} = \frac{\text{moles of products}}{\text{moles of hexose units in starting carbohydrates}} \times 100\%$$

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