



## Short Communication

## Effect of metal salts existence during the acid-catalyzed conversion of glucose in methanol medium

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## ABSTRACT

Catalytic effect of various metal sulfates as co-catalyst of extremely low sulfuric acid on glucose conversion in methanol medium was examined. The typical pathways included the alcoholysis of glucose into methyl glucoside and methyl levulinate, the formation of humin-type polymer from glucose or its degradation products, and the dehydration of methanol medium to dimethyl ether. The reaction selectivity is a clear function of the type of metal sulfates. Both  $K_2SO_4$  and  $Na_2SO_4$  can effectively suppress the further transformation of methyl glucoside from glucose, thus lower the polymer formation. For  $Fe_2(SO_4)_3$  and  $Al_2(SO_4)_3$ , methyl levulinate was formed in the highest yields.

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## 1. Introduction

Renewable biomass is a potential alternative to replace steadily depleting fossil resources in the chemical industry. Carbohydrates abundant in lignocellulosic biomass and agricultural residues are interesting precursors for a broad range of fine chemicals and fuels. However, inability to effectively and economically transform carbohydrates is still a major obstacle. In recent years, the development of chemical-catalytic approaches invites more and more concerns toward this challenging goal [1,2], among which the synthesis of bio-based chemicals in alcohol medium using an acid catalyst has been one of the focuses under study [3]. The target chemicals obtained mainly include esters like alkyl levulinate [4,5] and alkyl lactate [6], 5-alkoxymethylfurfural [7,8], and alkyl glucoside [9,10]. These bio-based chemicals found applications as fuels or fuel additives, solvents, biodegradable surfactants as well as substrates in the field of chemical synthesis [3,11,12].

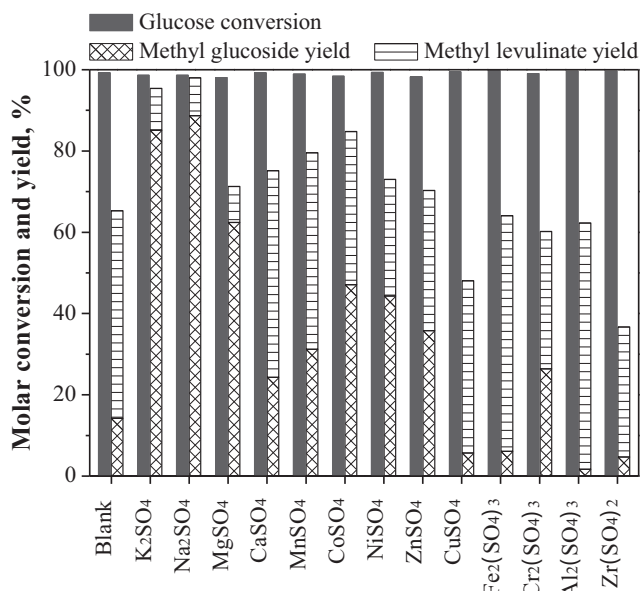
In the chemical-catalytic processing of carbohydrates into bio-based chemicals, metal salts were widely used as the catalyst. It can be found from literature that salts with Lewis acidity are more effective for the transformation of carbohydrates in most cases. For instance, Zhao

et al. discovered that  $CrCl_2$  was uniquely effective for the conversion of glucose in 1-alkyl-3-methylimidazolium chloride, giving a near 70% yield of 5-hydroxymethylfurfural [13]. Rasrendra et al. studied the catalytic effect of a wide range of chloride and sulfate salts on glucose conversion in water that was shown to affect the chemo-selectivity considerably. The major water-soluble product was lactic acid for Al (III) salts, and 5-hydroxymethylfurfural was formed in the highest yields by Zn (II) salts [14]. We employed metal chlorides to catalyze conversion of cellulose in water; 67% of levulinic acid was obtained by  $CrCl_3$  [15]. Zhou et al. recently showed that  $Al_2(SO_4)_3$  can serve as an efficient catalyst for the synthesis of methyl levulinate from carbohydrates including fructose, glucose, mannose, sucrose, cellobiose, starch, and cellulose [16]. The same authors also indicated that the catalyst system of  $SnCl_4$ -NaOH efficiently converts carbohydrates to methyl lactate [17]. Furthermore, catalyst systems consisting of Brønsted acids and salts were developed. Tominaga et al. reported the combination of  $In(OTf)_3$  and 2-naphthalenesulfonic acid as active catalysts for converting cellulose in methanol, where the yield of methyl levulinate reached 75% [18]. Beyond Lewis acidity salts, several studies also suggest that salts without Lewis acidity can promote carbohydrate conversion. For example, Potvin et al. reported that the addition of NaCl was efficient at increasing the yield of levulinic acid from cellulose in the presence of Nafion [19].

In our previous investigation, extremely low sulfuric acid catalyst system ( $\leq 0.01$  mol/L) is found to be a promising strategy for the conversion of glucose to bio-based chemicals in methanol medium,

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**Fig. 1.** Effect of various metal sulfates as co-catalyst of sulfuric acid on glucose conversion in methanol medium and liquid-phase product distribution. Reaction conditions: initial glucose concentration, 50 g/L; sulfuric acid concentration, 0.005 mol/L; metal sulfate concentration, 0.005 mol/L; temperature, 200 °C; and time, 2 h.

where methyl levulinate in around 50% yield was obtained, along with 14% of methyl glucoside [20]. To further improve the yield and selectivity of target products, on that basis, we here study the catalytic effect of a wide range of metal sulfates as co-catalyst of extremely low sulfuric acid on glucose conversion and undesired side-reaction in methanol medium under comparable conditions.

## 2. Results and discussion

### 2.1. Glucose conversion and liquid-phase product distribution

The effect of a wide range of different metal sulfates existence on the acid-catalyzed conversion of glucose in methanol medium was screened at 200 °C using a 50 g/L glucose solution with a sulfuric acid and metal sulfate concentration both of 0.005 mol/L as the co-catalyst. A single sulfuric acid was also employed as the catalyst for comparison. The influence of the presence of metal sulfates on the conversion of glucose after 2 h reaction time is shown in Fig. 1. It can be found that all metal sulfates lead effectively to glucose conversion of over 98%, and there were no significant differences with the blank group (without adding metal sulfates). To gain insights on the effect of metal sulfate existence on the chemo-selectivity of the reaction, the liquid-phase

products were identified and quantified by GC and IC analyses. The main reaction products including methyl glucoside and methyl levulinate were observed for all samples using various types of metal sulfates as the co-catalyst. Besides, trace amounts of other substances were detected, namely 5-methoxymethylfurfural, 5-hydroxymethylfurfural, 2-(dimethoxymethyl)-5-(methoxymethyl)furan and levulinic acid, and the determination of their detailed data is not presented here. The yields of methyl glucoside and methyl levulinate for various metal sulfates at 2 h reaction time are given in Fig. 1. It is clear that the product distribution was appreciably different in the presence of various metal sulfates. Of interest is the reaction for adding alkali metal sulfates (K<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub>) as the co-catalyst; the combined yield of methyl glucoside and methyl levulinate was up to 95%, which is remarkably higher than that for the individual sulfuric acid as the catalyst. The major product of the reaction was by far methyl glucoside, which accounts for around 90% of the product mixture, while methyl levulinate comprises only 10%. The comparison also clearly found that the selectivity of methyl levulinate is lower than that for the individual sulfuric acid. For this result, we conducted experiments with methyl glucoside instead of glucose as substrate under the same reaction conditions. It showed that methyl glucoside did not effectively translate into methyl levulinate in the presence of alkali metal sulfates (Table 1, entries 6–8). Further, when fructose was used as substrate, there was no significant difference in respect of fructose conversion and methyl levulinate yield between with and without alkali metal sulfates (Table 1, entries 9–11). The above results lead to the conclusion that alkali metal sulfates are more likely to suppress the isomerization of methyl glucoside to methyl fructoside, and resulted in low yield of methyl levulinate from glucose and methyl glucoside because the primary reaction pathway for methyl levulinate formation is involved through methyl fructoside [3]. However, there was no high yield of methyl glucoside to be obtained in the sole presence of alkali metal sulfates (without adding sulfuric acid), and their reaction performances were almost the same as that of no catalyst (Table 1, entries 1–3). Therefore, for high methyl glucoside yield and the combined yield obtained from glucose by combining sulfuric acid and alkali metal sulfates, it can be concluded that glucose can be almost quantitatively converted into methyl glucoside catalyzed by sulfuric acid in the reaction process [20], and alkali metal sulfates are used to stabilize methyl glucoside, thus lower the formation of other substances. For Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> as the co-catalyst, methyl glucoside was present in very small amounts and methyl levulinate was formed in the highest yields of 58% and 61%. Also, the sole Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> could provide methyl levulinate yields of 43% and 54% (Table 1, entries 4 and 5). The results suggest that the catalyst system consisting of both Lewis and Brønsted acid sites is more favorable for promoting the conversion of glucose to methyl levulinate. The total yields of methyl glucoside and methyl levulinate for the alkali earth metal sulfates (MgSO<sub>4</sub> and CaSO<sub>4</sub>) and several transition metal sulfates

**Table 1**  
Conversion of carbohydrates in methanol medium over various catalysts.

Entry	Substrate	Catalyst	Conversion, %	Yield, %			Dehydration rate of methanol to dimethyl ether, %
				Methyl glucoside	Methyl levulinate	Polymer	
1	Glucose	No	91	18	0	0	0
2	Glucose	K <sub>2</sub> SO <sub>4</sub>	93	21	0	0	0
3	Glucose	Na <sub>2</sub> SO <sub>4</sub>	94	24	0	0	0
4	Glucose	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	99	26	43	14	19
5	Glucose	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	100	9	54	17	23
6	Methyl glucoside	H <sub>2</sub> SO <sub>4</sub>	85	–	49	10	–
7	Methyl glucoside	H <sub>2</sub> SO <sub>4</sub> + K <sub>2</sub> SO <sub>4</sub>	7	–	5	1	–
8	Methyl glucoside	H <sub>2</sub> SO <sub>4</sub> + Na <sub>2</sub> SO <sub>4</sub>	6	–	4	1	–
9	Fructose	H <sub>2</sub> SO <sub>4</sub>	100	–	85	12	–
10	Fructose	H <sub>2</sub> SO <sub>4</sub> + K <sub>2</sub> SO <sub>4</sub>	100	–	82	11	–
11	Fructose	H <sub>2</sub> SO <sub>4</sub> + Na <sub>2</sub> SO <sub>4</sub>	100	–	84	12	–

Reaction conditions: substrate concentration, 50 g/L; sulfuric acid concentration, 0.005 mol/L; metal sulfate concentration, 0.005 mol/L; temperature, 200 °C; and time, 2 h.

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