Catalytic Decomposition of Glucose to Levulinic Acid by Synergy of Organic Lewis Acid and Brønsted Acid in Water

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Four organic Lewis acids, samarium(III), aluminum(III), yttrium(III), and indium(III) trifluoromethanesulfonates were combined with four organic Brønsted acids, benzenesulfonic, toluene-p-sulfonic, trichloroacetic, and oxalic acids to synergistically catalyze the decomposition of glucose to produce levulinic acid (LA). The combination of aluminum trifluoromethanesulfonate ($Al(CF_3SO_3)_3$) and oxalic acid ($H_2C_2O_4$) exhibited a strong synergic activity for the decomposition of glucose to LA. The effects of the mole fraction of $Al(CF_3SO_3)_3$ in the $Al(CF_3SO_3)_3$-$H_2C_2O_4$ system on the decompositions of glucose, fructose, and 5-hydroxymethylfurfural (5-HMF) were investigated. The mixed-acid system showed the strongest synergic catalytic activity for glucose, fructose, and 5-HMF decompositions at the $Al(CF_3SO_3)_3$ mole fraction of 0.33. The effect of temperature on the decomposition of glucose in the $Al(CF_3SO_3)_3$-$H_2C_2O_4$ system was also investigated. Based on the results obtained in this contribution and previous work, synergy in catalytic systems was demonstrated.

Keywords: Glucose; Levulinic acid; Organic Lewis acid; Organic Brønsted acid

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INTRODUCTION

As fossil resources are steadily being depleted, deriving chemicals and fuels from biomass to supplement fossil resources is becoming increasingly important. Levulinic acid (LA), a building block for producing hydrocarbon liquid fuels (Bozell 2000; Nilges *et al.* 2012), valeric esters (Geilen *et al.* 2010; Serrano-Ruiz *et al.* 2012), fuel additives, as well as a variety of chemicals (Serrano-Ruiz *et al.* 2010; Lin *et al.* 2012), has been regarded as one of the top 10 building blocks for the biorefinery industry (Bozell and Petersen 2010). LA can be prepared from cellulose (Van de Vyver *et al.* 2011), which is the most abundant biomass in the world (Deng *et al.* 2010; Tao *et al.* 2011; Wu *et al.* 2012). It could be a critical bridge linking biomass and a variety of high-demand chemicals and fuels.

In the last two decades, the decomposition of cellulose to produce LA has attracted much attention (Van de Vyver *et al.* 2011; Weingarten *et al.* 2012b). Brønsted acids such as sulphuric acid are widely regarded as an effective catalyst for this reaction (Girisuta *et al.* 2008; Weingarten *et al.* 2012a). The relatively low yield of LA and the formation of humins, however, have limited the progress of LA in industry even as attempts to improve LA selectivity have ceaselessly continued. For probing the mechanism of the formation of LA and other products to provide insights for the process of LA production from cellulose, pure sugars were employed as model compounds in many studies (Weingarten *et al.* 2013; Qi *et al.* 2014). Recently, Choudhary *et al.* (2013) proposed a synergic catalytic mechanism for the $CrCl_3$-HCl system for the decomposition of glucose to 5-HMF and LA, in which the Lewis acid more effectively catalyzes the isomerization of glucose than the Brønsted acid. Extending to other combinations of inorganic Lewis and Brønsted acids, the authors (Yang *et al.* 2013) found that the $CrCl_3$-H_3PO_4 system had a strong synergic catalytic activity for the decomposition of glucose to LA, and the fraction of $CrCl_3$ to show strongest synergic catalytic activity was about 0.5. Although the synergic catalysis mechanisms on the inorganic Lewis and Brønsted acids were demonstrated, the behaviors of the catalytic system of organic Lewis and Brønsted acids are still unclear. Studies on unknown catalytic systems would be helpful for advancements in the commercial production of LA.

Metal triflates, which have strong Lewis acidity and great thermal and chemical stability, show efficient catalytic activities in pure water (Kobayashi *et al.* 2002). Therefore, the investigated mixed-acid systems were extended to organic acids in this article. The mixed-acid systems of four organic Lewis acids, samarium(III), aluminum(III), yttrium(III), and indium(III) trifluoromethanesulfonates ($Sm(CF_3SO_3)_3$, $Al(CF_3SO_3)_3$, $Y(CF_3SO_3)_3$, and $In(CF_3SO_3)_3$) combined with four organic Brønsted acids, benzenesulfonic, toluene-p-sulfonic, trichloroacetic, and oxalic acids ($C_6H_6O_3S$, $C_7H_8O_3S$, Cl_3CCOOH, and $H_2C_2O_4$) were evaluated for the decomposition of glucose to produce LA. The effects of the fraction of $Al(CF_3SO_3)_3$ in the $Al(CF_3SO_3)_3$-$H_2C_2O_4$ system on the decompositions of glucose, fructose and 5-hydroxymethylfurfural (5-HMF) were investigated. The effect of temperature on the decomposition of glucose in the $Al(CF_3SO_3)_3$-$H_2C_2O_4$ system was also investigated. Based on the results obtained in this study and the previous work, the synergic catalysis mechanisms were explored.

EXPERIMENTAL

Materials

Samarium(III) trifluoromethanesulfonate (≥98%), aluminum(III) trifluoro-methane-sulfonate (≥ 99%), and anhydrous oxalic acid (≥ 98%) were purchased from Alfa Aesar Company. Trichloroacetic acid (≥99%) was obtained from Sinopharm Chemical Reagent Co. Ltd., China. Glucose (99%) and levulinic acid (99%) were purchased from Aladdin chemistry Co., Ltd. Fructose (≥95%), 5-hydroxymethylfurfural (≥ 98%), and benzenesulfonic acid (≥95%) were purchased from J&K chemica Ltd. Yttrium(III) trifluoromethanesulfonate (≥98%) and indium(III) trifluoromethanesulfonate (≥ 99%) were obtained from Strem Chemicals, Inc. Toluene-p-sulfonic acid (≥99%) was purchased from Fluorochem Ltd. Deionized water was made in house.

Reactor

The batch reactor, made of stainless steel, had a volume of about 100 mL. A teflon (polytetrafluoroethylene, PTFE) cup was inserted inside the reactor to prevent the corrosion of acids and the wall effect of metal ions. The reactor was heated by a furnace (capable of heating up to 5 reactors). The furnace has a precise temperature control and can maintain temperatures to within 1%.

Experimental Procedure

Glucose, fructose, or 5-HMF was dissolved in deionized water at 0.0556 mol/L. A carefully measured amount of Lewis acid and Brønsted acid was added into the aqueous solutions of glucose, fructose, or 5-HMF, and the acid concentration of pure Brønsted acid, pure Lewis acid, or mixed acids was 0.015 mol/L. Then 25 mL of the aqueous solution of reactant and catalysts was added to the reactor. After being sealed, the reactor was placed into the furnace, which had been preheated to the desired temperature. The reactor was removed from the furnace at fixed time intervals and quickly put into cool water to quench the reaction. The sample was collected from the cooled reactor, rinsed to a 50 mL volumetric flask with deionized water, and diluted to 50 mL with deionized water.

Analysis Methods

The solution in the flask was quantitatively analyzed by HPLC (Agilent 1100) with an RID detector. The HPLC column was Sugar SH1011 (Shodex, 8.0 mm ID×300 mmL). The mobile phase was 0.5×10^{-3} mol/L H_2SO_4, and the flow rate was 0.5 mL/min. The temperatures of the column and RID detector were 60 and 40 °C, respectively. The injection volume was 10 μL.

The yield of LA was calculated by the following formula:

$$\text{LA yield} = \frac{\text{amount of LA (mol) produced}}{\text{amount of glucose, fructose or 5-HMF (mol) added}} \times 100\% \quad (1)$$

A synergy factor was defined to evaluate the synergic activity in the mixed-acid systems, and Fig. 1 shows the definition of *A* and *B* in relation to the synergy factor.

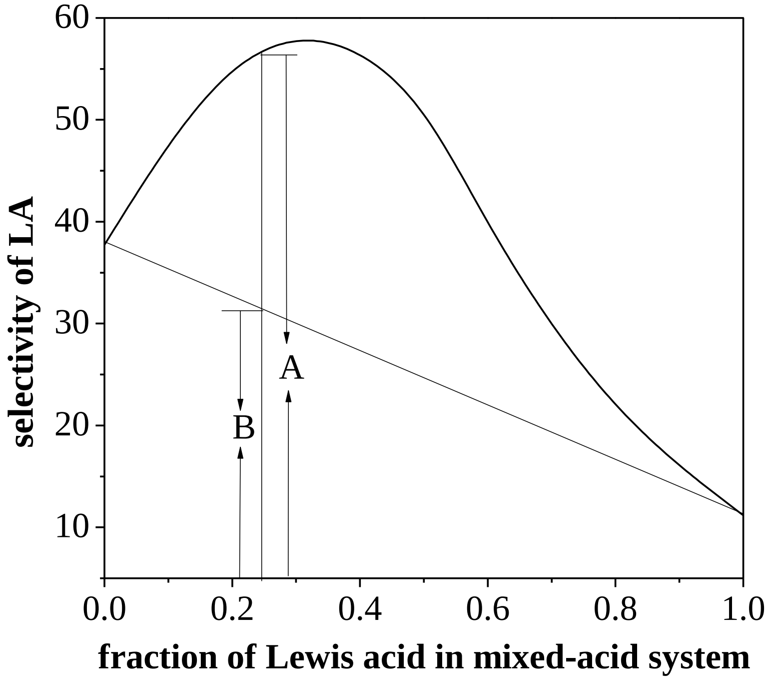

Fig. 1. The definition of A and B related to synergy factor in mixed-acid system

The quantity *A* represents the selectivity of LA obtained in the mixed-acid system. The quantity *B* is the mole fraction of Brønsted acid in the mixed system times the selectivity of LA catalyzed by pure Brønsted acid plus the mole fraction of Lewis acid in the mixed-acid system times the selectivity of LA catalyzed by the pure Lewis acid. *B* represents the theoretical selectivity of LA in the mixed-acid system. The trend line connecting the values of LA selectivity with pure Brønsted acid and Lewis acid represents the theoretical value of LA selectivity at any fraction of Brønsted to Lewis acid in the mixed-acid system. When the fraction of Brønsted to Lewis acid in the mixed-acid system is fixed, the theoretical selectivity of LA in the mixed-acid system can be identified on the trend line.

$$\text{Synergy factor} = A / B \tag{2}$$

If the synergy factor of the mixed-acid system is larger than 1, it means that the mixed-acid system has a positive synergic catalytic activity.

RESULTS AND DISCUSSION

Evaluation of Mixed-acid Systems on Glucose Decomposition to LA

Table 1 shows the conversion of glucose, yield of LA and 5-HMF, and selectivity of LA of glucose decomposition with four organic Brønsted acids, $C_6H_6O_3S$, $C_7H_8O_3S$, Cl_3CCOOH, and $H_2C_2O_4$ combined with trifluoromethanesulfonate acid at 180 °C for 5 h.

The molar concentration of pure Brønsted acid or Lewis acid was 0.015 mol/L. Correspondingly, in the mixed-acid systems, the molar concentration of the Brønsted acids was 0.01 mol/L, and the molar concentration of the Lewis acids was 0.005 mol/L. When glucose was decomposed with 0.015 mol/L of $H_2C_2O_4$ at 180 °C for 5 h, the yield and selectivity of LA were only 3.3% and 7.1%, respectively. With pure $Al(CF_3SO_3)_3$, the yield and selectivity of LA were both 9.8%. In comparison, the yield and selectivity of LA were significantly increased to 39.9% and 39.9% respectively, in the $Al(CF_3SO_3)_3$-$H_2C_2O_4$ system.

Similar phenomena were found in the other trifluoromethanesulfonate acid-$H_2C_2O_4$ system. In contrast, most other systems showed lower yields and selectivities than pure organic Brønsted acid.

To give a clearer representation of the effect of catalytic synergy on the decomposition of glucose, a synergy factor (formula shown in experimental section) was defined. If the synergy factor of the mixed-acid system is larger than 1, then the mixed-acid system has a positive synergic catalytic activity.

Figure 2 shows the synergy factor of each mixed-acid system. The combinations of trifluoromethanesulfonate acids and $H_2C_2O_4$ all showed high synergy factors (>4), suggesting that $H_2C_2O_4$ and trifluoromethanesulfonate acids had strong synergic effects. Based on the low synergy factors, the other systems had no obvious synergic effect. Among them, the $Al(CF_3SO_3)_3$ - $H_2C_2O_4$ system had the largest synergy factor (5.0) and was selected for further study.

Table 1. Conversion of Glucose, Yield of LA, and 5-HMF for Glucose Decomposition with $Al(CF_3SO_3)_3$ Combining $C_6H_6O_3S$, $C_7H_8O_3S$, Cl_3CCOOH, or $H_2C_2O_4$ at 180 °C for 5 h. (Concentration: pure Brønsted acid or Lewis acid = 0.015 mol/L, in mixed-acid system: Brønsted acid = 0.01 mol/L, Lewis acid = 0.005 mol/L; glucose = 0.0556 mol/L)

Entry	Lewis acid	Brønsted acid	Glucose conv./%	LA yield/%	LA sele. /%	5-HMF yield/%
1	/	/	50.3	0.0	0.0	22.1
2	$Sm(CF_3SO_3)_3$	/	100	10.4	10.4	0.0
3	$Al(CF_3SO_3)_3$	/	100	9.8	9.8	0.0
4	$Y(CF_3SO_3)_3$	/	100	13.5	13.5	0.0
5	$In(CF_3SO_3)_3$	/	100	15.8	15.8	0.0
6	/	$C_6H_6O_3S$	73.2	30.8	42.0	3.2
7	/	$C_7H_8O_3S$	73.2	32.0	43.6	3.2
8	/	Cl_3CCOOH	57.0	19.1	33.5	5.6
9	/	$H_2C_2O_4$	47.0	3.3	7.1	15.4
10	$Sm(CF_3SO_3)_3$	$C_6H_6O_3S$	100	29.3	29.3	0.0
11	$Al(CF_3SO_3)_3$	$C_6H_6O_3S$	100	17.3	17.3	0.0
12	$Y(CF_3SO_3)_3$	$C_6H_6O_3S$	100	31.5	31.5	0.0
13	$In(CF_3SO_3)_3$	$C_6H_6O_3S$	100	33.7	33.7	0.0
14	$Sm(CF_3SO_3)_3$	$C_7H_8O_3S$	100	27.2	27.2	1.6
15	$Al(CF_3SO_3)_3$	$C_7H_8O_3S$	100	16.6	16.6	0.0
16	$Y(CF_3SO_3)_3$	$C_7H_8O_3S$	99.4	29.9	30.1	0.0
17	$In(CF_3SO_3)_3$	$C_7H_8O_3S$	100	15.5	15.5	0.0
18	$Sm(CF_3SO_3)_3$	Cl_3CCOOH	99.7	14.4	14.5	1.30
19	$Al(CF_3SO_3)_3$	Cl_3CCOOH	100	11.7	11.7	0.0
20	$Y(CF_3SO_3)_3$	Cl_3CCOOH	99.8	16.7	16.8	1.2
21	$In(CF_3SO_3)_3$	Cl_3CCOOH	100	41.4	41.4	0.0
22	$Sm(CF_3SO_3)_3$	$H_2C_2O_4$	76.6	30.2	39.5	4.0
23	$Al(CF_3SO_3)_3$	$H_2C_2O_4$	100	39.9	39.9	0.0
24	$Y(CF_3SO_3)_3$	$H_2C_2O_4$	79.6	30.7	38.6	4.0
25	$In(CF_3SO_3)_3$	$H_2C_2O_4$	99.9	41.6	41.7	0.0

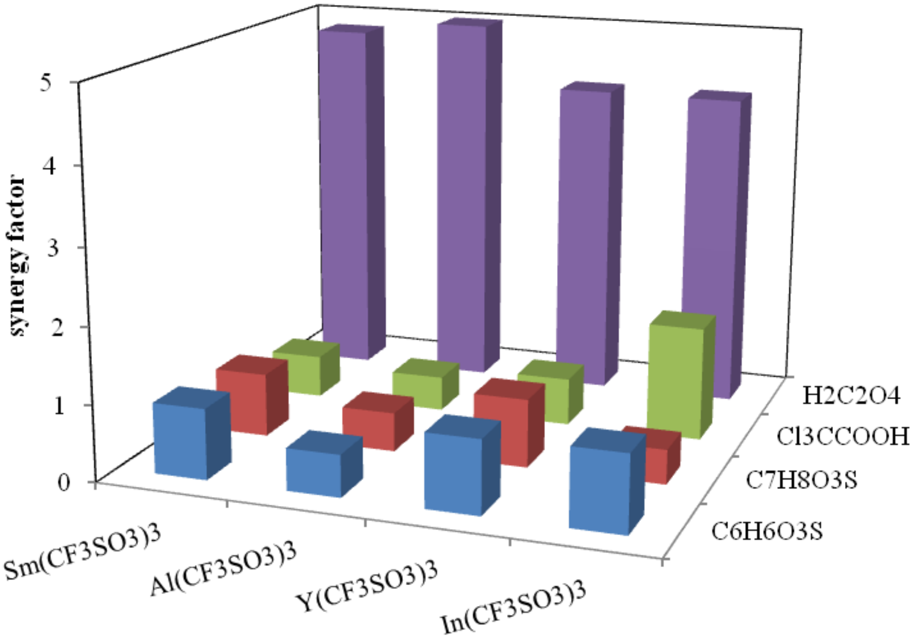

Fig. 2. Synergy factors for glucose decomposition with organic Brønsted acid and Lewis acid at 180 °C for 5 h. Concentration in mixed-acid system: Brønsted acid = 0.01 mol/L, Lewis acid = 0.005 mol/L, glucose = 0.0556 mol /L.

Effect of Fraction of $Al(CF_3SO_3)_3$ in the $Al(CF_3SO_3)_3$- $H_2C_2O_4$ System on Glucose, Fructose, and 5-HMF Decomposition to LA

A three-step reaction pathway for the decomposition of glucose to LA has been summarized in the literature: isomerization of glucose to fructose, dehydration of fructose to 5-HMF, and decomposition of 5-HMF to LA (Zhao *et al.* 2007). In order to study the synergic catalytic behavior of $H_2C_2O_4$ and $Al(CF_3SO_3)_3$ on glucose decomposition to LA, experiments using glucose, fructose, and 5-HMF as reactants were carried out. Figure 3 shows the effect of the fraction of $Al(CF_3SO_3)_3$ in the mixed-acid system on the decomposition of glucose, fructose, and 5-HMF to LA. The total molar concentrations of the acids were always maintained at 0.015 mol/L.

In Fig. 3a, the conversions of fructose were all 100%, meaning that fructose was completely consumed during the heating period. The conversions of glucose and 5-HMF both increased to 100% as the fraction of $Al(CF_3SO_3)_3$ increased. In Fig. 3c, the yield of LA from glucose was only 3.3% with 0.015 mol/L of $H_2C_2O_4$ (the fraction of $Al(CF_3SO_3)_3$ was 0) at 180 °C for 5 h, while the yield of LA significantly increased with the increase of the $Al(CF_3SO_3)_3$ fraction. The highest yield of LA (39.9%) was achieved at the $Al(CF_3SO_3)_3$ fraction of 0.33. In contrast, when the $Al(CF_3SO_3)_3$ fraction was zero, the yield of LA from fructose was 23%, much higher than the yield obtained from glucose. Although the yield of LA from fructose was significantly higher than that of glucose with pure $H_2C_2O_4$, the difference in LA yield shrank as the fraction of $Al(CF_3SO_3)_3$ increased. The yields of LA from glucose and fructose were almost the same among the $Al(CF_3SO_3)_3$ fractions of 0.45 to 1. Similar behaviors were found in the selectivities of LA from glucose and fructose (Fig. 3d). The yields of LA from 5-HMF are always higher than those from glucose and fructose at the same reaction condition. The overall trend discovered for the yield of LA from 5-HMF was an initial increase and then decrease as the fraction of $Al(CF_3SO_3)_3$ was increased.

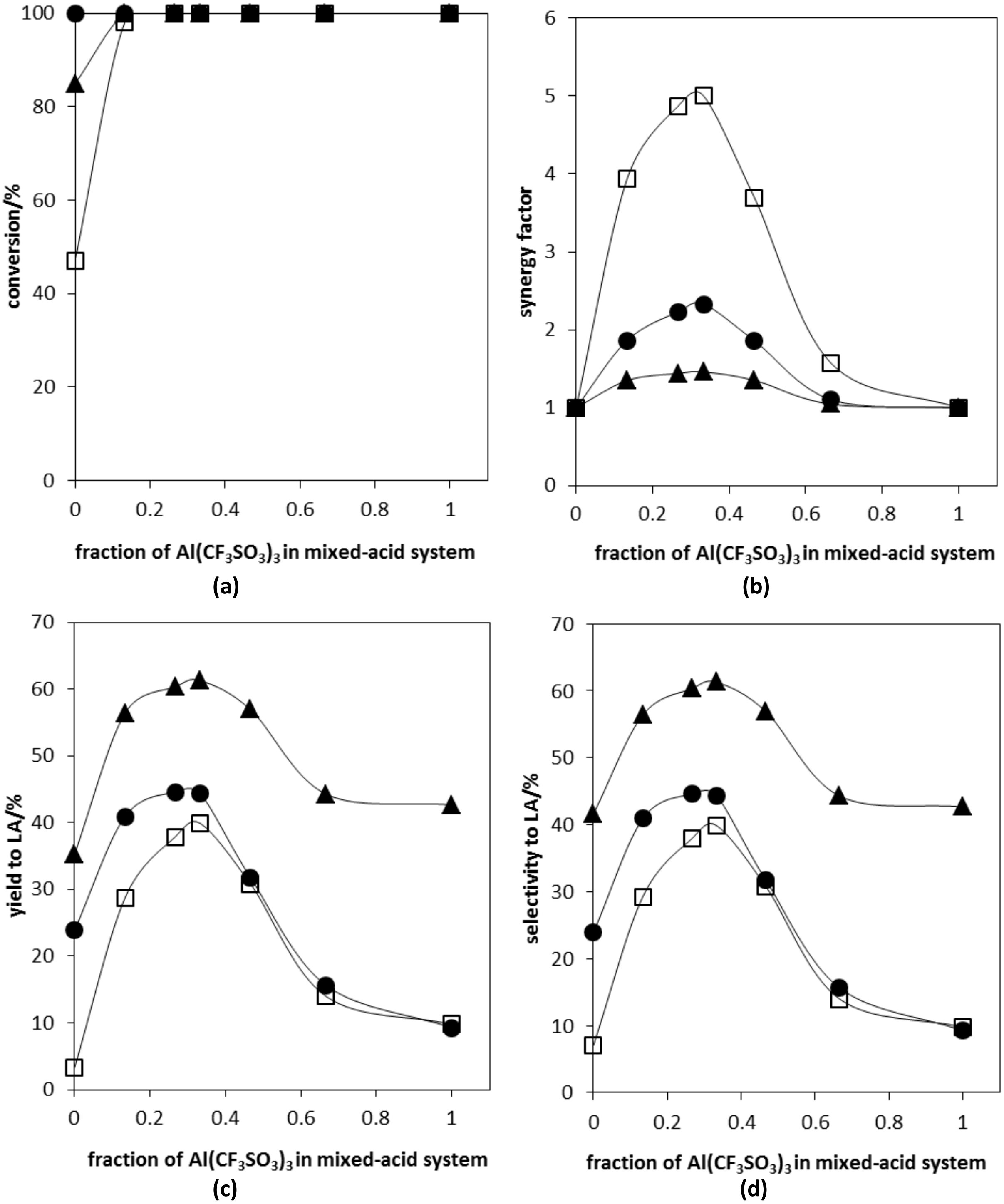

Fig. 3. Conversions of glucose, fructose, and 5-HMF, yields to LA, selectivities to LA, and synergy factors in hydrothermal decomposition. Reaction condition: concentration of glucose, fructose, or 5-HMF = 0.0556 mol/L, concentration of $Al(CF_3SO_3)_3 + H_2C_2O_4$ = 0.015mol/L, temperature = 180 °C, reaction time = 5 h. □-glucose, ●-fructose, ▲-5-HMF

As can be seen in Figs. 3c and 3b, the selectivity of LA and synergy factor for glucose, fructose, and 5-HMF also had a maximum value at the $Al(CF_3SO_3)_3$ fraction of 0.33. The selectivity of LA obtained under these conditions also exhibited the trend of first increasing then decreasing as the $Al(CF_3SO_3)_3$ fraction was increased, illustrating the synergy between $Al(CF_3SO_3)_3$ and $H_2C_2O_4$.

Effect of temperature on glucose decomposition to LA

Figure 4 shows the conversion of glucose, yield of LA, and selectivity of LA for the decomposition of glucose in the $Al(CF_3SO_3)_3$-$H_2C_2O_4$ system at the temperatures of 160, 170, 180, and 190 °C for 5 h. The concentration of $Al(CF_3SO_3)_3$ was 0.005 mol/L and concentration of $H_2C_2O_4$ was 0.010 mol/L. The conversion of glucose increased as the temperature rose, but the selectivity and yield of LA were not significantly impacted by temperature in the temperature range of 170 to 190 °C. The decrease in 5-HMF yield with the rise in temperature signaled that high temperatures facilitated the decomposition of 5-HMF. Overall, temperature was not a critical factor for the synergic catalysis with respect to the effects of catalyst synergy.

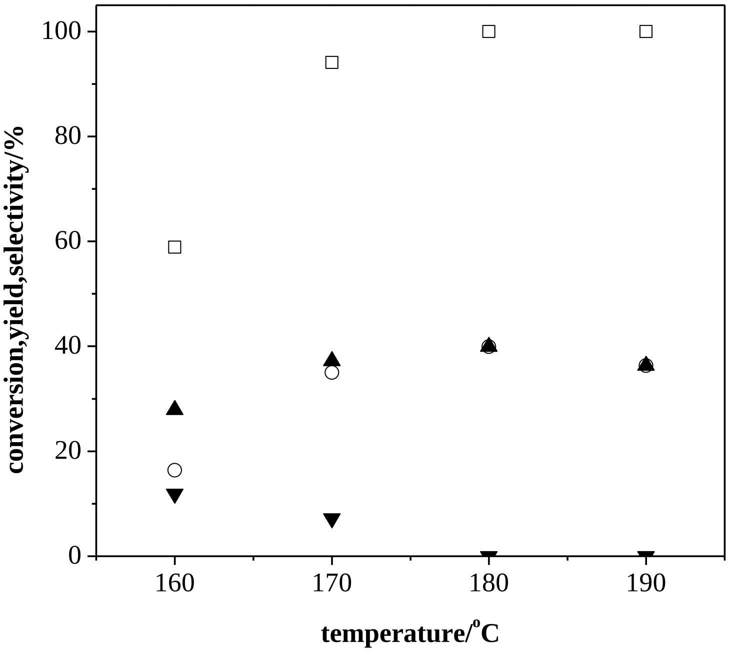

Fig. 4. Conversion of glucose, yield of LA, and selectivity of LA for decomposition of glucose in $Al(CF_3SO_3)_3$- $H_2C_2O_4$ system at different temperatures. Reaction condition: concentration of $Al(CF_3SO_3)_3$ =0.005mol/L, concentration of $H_2C_2O_4$ = 0.010mol/L, concentration of glucose = 0.0556 mol/L, and reaction time = 5 h. □-conversion of glucose, ○- yield of LA, ▲- selectivity of LA, ▼- yield of 5-HMF

Synergic Catalysis Mechanism for Glucose Decomposition to LA

The decomposition of glucose to LA and formic acid is a multi-step reaction involving the isomerization of glucose to fructose, dehydration of fructose to 5-HMF, and the hydrolysis of 5-HMF to LA and formic acid. Past studies have found that although both Brønsted and Lewis acids catalyze the overall reaction, specific steps in the reaction process are more efficiently catalyzed by different types of acids. Table 1 shows that the conversions of glucose with Lewis acids were all 100%, but those with Brønsted acid were not, indicating that Lewis acids are more effective for promoting the isomerization of glucose to fructose. While most Brønsted acids result in a higher selectivity for LA than Lewis acids, oxalic acid is a noteworthy exception. Its particularly low selectivity for LA is likely due to the fact that it decomposes into formic acid at 180 °C, meaning that Brønsted acids are better catalysts for the following dehydration and hydrolysis steps. Because Brønsted and Lewis acids play different roles and make different contributions to the multi-step reaction from glucose to LA, combining the two to take advantage of both their strengths may result in a synergic effect.

From the calculated synergy factor, it was found that oxalic acid had good synergistic effects with $Sm(CF_3SO_3)_3$, $Al(CF_3SO_3)_3$, $Y(CF_3SO_3)_3$, and $In(CF_3SO_3)_3$, and the selectivity for LA was much higher than when only pure Lewis or Brønsted acid was used. Although oxalic acid by itself decomposes at high temperatures, oxalic acid probably forms a relatively stable complex with triflates that inhibits its decomposition and increases the concentration of H^+, thereby improving the selectivity for LA. Furthermore, the optimum fraction of the $Al(CF_3SO_3)_3$-$H_2C_2O_4$ system was found to be 1:2, while that of the H_3PO_4-$CrCl_3$ system was 1:1 (Yang *et al.* 2013), meaning that the triflate oxalic acid system requires only half as much Lewis acids. This may be due to the greater stability of $Al(CF_3SO_3)_3$ in water than traditional Lewis acids such as $AlCl_3$ and $CrCl_3$, which tend to partially hydrolyze in water. $Al(CF_3SO_3)_3$ also possesses high thermal and chemical stabilities, and so the molar fraction of $Al(CF_3SO_3)_3$ needed to reach the highest yield is smaller than that of traditional Lewis acids.

CONCLUSIONS

1. The combination of aluminum trifluoromethanesulfonate ($Al(CF_3SO_3)_3$) and oxalic acid ($H_2C_2O_4$) exhibited a strong synergic activity for the decomposition of glucose to levulinic acid (LA).
2. The mixed-acid system showed the strongest synergic catalytic activity for glucose, fructose, and 5-hydroxymethylfurfural (5-HMF) decompositions at the $Al(CF_3SO_3)_3$ fraction of 0.33.
3. Temperature was not the critical factor in the synergy of the catalysts.
4. Based on the results obtained in this study and previous work, the synergic catalysis mechanisms were demonstrated.

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