



Short communication

Novelty catalytic transformation of sugar over excellent biphasic-heterogeneous reaction system

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ABSTRACT

Highly selective production of 5-ethoxymethylfurfural (EMF) from transformation of glucose in ultrasound-assisted biphasic system over metal (Al, Zn or Ni)-doped sulfonated carbon (SC) catalyst was studied in details. It was found that EMF selectivities of 12.8, 84.4, 85.1 and 32.8% could be obtained from SC, Al-SC, Zn-SC and Ni-SC, respectively. The effect of ultrasonic application indicated that EMF was easily produced via isomerization, dehydration and etherification. Moreover, low leaching amount of metal species was found for Zn-SC, resulting in better recyclability when compared with Al-SC. This research provided a novel way for EMF production with high selectivity at short reaction.

1. Introduction

The application of renewable resources has attracted great attention in recent years since the consumption of fossil fuels derived from resources such as oil, coal, natural gas increased with many environmental problems associated. Biomass has been regarded as a renewable resource due to the progressive depletion of conventional fossil fuels which can be possibly converted into energy-fuels such as gas and liquid chemical fuels [1]. The conversion of biomass resources into biofuels over novelty green catalysts is presented to be one of the major challenges in the field of environmental chemistry or chemical engineering. Recently, the transformation of some carbohydrates such as glucose and fructose into important chemical building blocks, additive petroleum fuels such as 5-hydroxymethylfurfural (HMF), 5-ethoxymethylfurfural (EMF), levulinic acid (LA), ethyl levulinate (EL) and formic acid (FA) have been attracted much interest [2]. Among of them, EMF can be potentially regarded as one of high value-added chemicals that can be applied as chemical intermediates or fuel additives [3].

Selective conversion of carbohydrate-derived glucose into EMF was studied by using several kinds of acid catalysts [4–7]. Recently, Zuo et al. [7] obtained EMF yield (48%) from transformation of glucose using co-catalyst of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ with H_2SO_4 . They also reported that glucose isomerization/epimerization processes should be catalyzed by Lewis-acid site at first step, and followed by Brønsted-acid site for fructose dehydration. Yang et al. found that EMF production from glucose conversion was difficult when compared with fructose

substrate. Here, fructose could be easily converted into EMF over homogeneous H_2SO_4 catalyst, providing ~35% of EMF yield [8]. Interestingly, the formation of by-products such as EL and polymer humins were remarkably obstructed while yield of EMF was exceptionally enhanced over SO_3H -ionic liquid, which reported by Kraus et al. [9]. Meanwhile, some ionic liquids such as AlCl_3 and BMIMCl are also identified as the excellent Lewis-acid homogeneous catalyst for isomerization, dehydration and polymerization reactions [10,11]. However, considering on application of industrial-practical process with environmental friendly, a lot of problems occurred such as toxicity, expensive, corrosiveness and hard separation procedure as well as difficulty in recycling should be solved from now [12–14]. Up to date, several kind of heterogeneous catalysts are largely applied for EMF production [15–17]. Meanwhile, to complete the reaction, 2-step EMF synthesis and long reaction time are required, resulting in high production cost.

Therefore, it is necessary to develop the novel reaction system using high performance/stability of heterogeneous catalyst which has lower cost, higher activity and better stability than commercial catalyst. From mentioned above, selective conversion of glucose into EMF was applied using ultrasonic-assisted biphasic reaction system. Here, reaction rate could possibly improve by the number of cavitation bubbles formed in the medium and energy generated due to cavitation which could improve the process of interfacial area or mass transfer on the substrate towards a fast reaction rate, expecting to the improving in EMF formation efficiency. The catalyst was prepared via impregnation, pyrolysis and sulfonation [18]. The physical and chemical properties of as-

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synthesized catalyst were investigated in details. Moreover, the reusability of catalyst was also performed.

2. Experimental

2.1. Catalyst preparation

In brief, 10 g of biomass was impregnated with a certain amount (5 wt% metal) of AlCl_3 , ZnCl_2 or NiCl_2 (Sigma-Aldrich) solution, and stirred for 12 h. Here, biomass or waste wood derived from wood processing plant was used as a carbon feedstock. Then, it was evaporated at 80°C for 6 h. The as-prepared sample was pyrolyzed at 650°C for 2 h. Next step, sulfonation process was carried out at 150°C for 24 h using concentrated sulfuric acid (Merck) as sulfonic source. Here, the mass ratio of H_2SO_4 to sample (3 to 1) was applied in this synthesis which selected from our preliminary study. Thereafter, the obtained catalyst was filtered, washed for several times with distilled water and ethanol to remove excess sulfate ions and finally dried in vacuum oven at 110°C for overnight. Here, it should be noted that SC doped with AlCl_3 , ZnCl_2 and NiCl_2 were named as Al-SC, Zn-SC and Ni-SC, respectively. Details of catalyst characterization methods (e.g., BET, XRD, SEM-EDS and titration) are provided in the Supporting Information (SI).

2.2. Catalytic performance

The catalytic upgrading of glucose was carried out in a three-neck round bottom flask equipped with a reflux condenser and an ultrasonic probe as well as a thermocouple thermometer. A schematic diagram of the experimental setup was shown in Fig. S1. In each experiment, an ultrasonic power of 85 W, a frequency of 40 kHz and a stirring speed at 600 rpm were applied. In a typical run, 0.5 g of glucose (Ajax Finechem), 20 mL of ethanol (99% Fisher BioReagents), 5 mL of distilled water, 1.5 g of NaCl (Ajax Finechem), 20 mL of tetrahydrofuran (99.9%, Sigma-Aldrich), and required amount of THF and catalyst reactor was added into reactor. Then, reaction system were conducted at 106°C for 72 min based on optimization processes. After finishing reaction, the mixture product was cooled in an ice-bath, diluted and filtered with a $0.22\ \mu\text{m}$ syringe filter. Before reuse in each cycle, the separated spent catalyst was washed with DI water and acetone for several times in order to eliminate some by-products prior, and then dried at 105°C for overnight [19]. The glucose and the formed products were analyzed by an Agilent 1200 HPLC chromatograph equipped with an Aminex HPX-87H column as well as refractive index and UV detectors. 0.5 mM H_2SO_4 solution was utilized as mobile phase at column temperature of 60°C with a total flow rate of 0.6 mL/min. The conversion of substrate and the selectivity of each product were analyzed using an external standard method, and calculated according to Eqs. (1) and (2):

$$\text{Glucose conversion (\%)} = \frac{\text{Mole percentage of glucose reacted}}{\text{Mole percentage of initial glucose}} \times 100 \quad (1)$$

$$\text{Product selectivity (\%)} = \frac{\text{Mole percentage of product produced}}{\text{Mole percentage of glucose reacted}} \times 100 \quad (2)$$

3. Results and discussion

Here, the total evidences with discussion on the results of catalyst characterization and kinetic experimental studies are provided in SI. To evaluate the metal-SC as a promising catalyst for further application in practical process, comparing their catalytic perfume with each commercial solid acid catalyst were tested under obtained optimum conditions: catalyst amount of 62 mg, reaction time of 72 min, reaction temperature of 106°C and THF amount of 250 mmol. As shown in

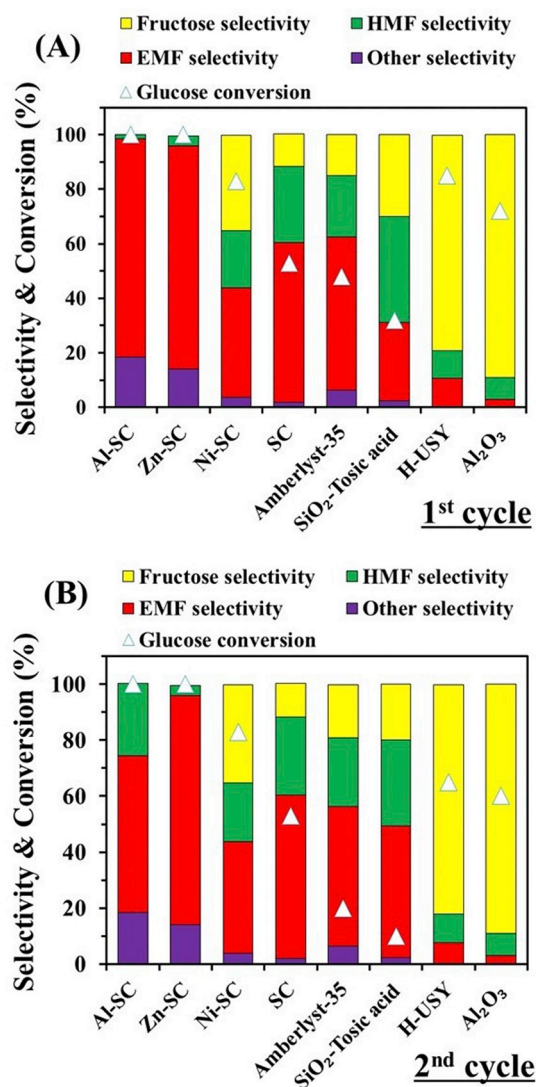


Fig. 1. Comparison of catalytic conversion of glucose into EMF over various solid acid catalysts (A) 1st cycle and (B) 2nd cycle in ultrasonic system.

Fig. 1A, Al-SC and Zn-SC presented excellent performance for glucose transformation with EMF selectivity ($>80\%$). The conversion rate of glycerol into EMF product was in the order of $\text{Zn-SC} > \text{Al-SC} > \text{SC} > \text{Amberlyst-35} > \text{Ni-SC} > \text{SiO}_2\text{-Tosic acid} > \text{H-USY} > \text{Al}_2\text{O}_3$. High selectivity for fructose formation was clearly found in H-USY and Al_2O_3 , which could be attributed to the existence of only Lewis acid site for glucose isomerization. This indicates that contribution of Brönsted acid and Lewis acid sites is very important. Fig. 2 shows the NH_3 -TPD profiles of Al-SC, Zn-SC and Ni-SC. One can see that NH_3 desorption peaks appeared at low temperature ($\sim 230^\circ\text{C}$) and high temperature ($\sim 415^\circ\text{C}$) were should be attributed to the weak/Lewis acid and strong/Brönsted acid sites, respectively. Interestingly, Al-SC presented the existence of strong acid site with high amount while NH_3 -TPD result of Zn-SC was contrasting.

Based on glucose conversion with compared various catalysts, Zn-SC could be excellently reused while Amberlyst-35, were evidently deactivated after second reuse cycle (Fig. 1B), suggesting to the athletic adsorption of hydrophilic-oligomeric of by-products and the unstudied leaching of sulfonic group [20]. Moreover, the presence of strongly hydrophilic properties which favored to selectivity create an appropriate environment for adsorption of H_2O , resulting in the poor long-term reusability. In case of as-prepared catalyst, it is well known that the outer layer of the catalyst structure consisted of active sites with

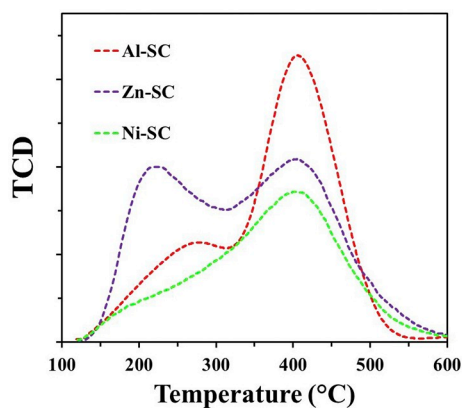


Fig. 2. NH_3 -TPD profiles of Al-SC, Zn-SC and Ni-SC.

Table 1

Comparison of EMF yield derived from glucose conversion using different catalysts.

Catalyst	Condition	EMF (%)	Ref.
Sn-beta	Hydrothermal system: 125 °C for 6 h	29.0	[3]
Amberlyst-15- CrCl_3	Reflux system: 130 °C for 2 h	46.7	[7]
AlCl_3	Hydrothermal system: 100 °C for 11 h	38.4	[11]
MIL-101- SO_3H	Hydrothermal system: 130 °C for 15 h	~8.0	[16]
OMC- SO_3H	Hydrothermal system: 100 °C for 15 h	0.9	[25]
Al-SC	Ultrasonic system: 106 °C for 72 min	84.4	[This work]
Zn-SC	Ultrasonic system: 106 °C for 72 min	85.1	[This work]

hydrophilic groups such as $-\text{SO}_3\text{H}$, $-\text{COOH}$ and phenolic $-\text{OH}$ groups while the inner layer consists of hydrophobic groups such as polyaromatics C—C, which could facilitate the effect of mass transfer, leading to better catalytic performance and stability [21,22]. Also, even though the acidity of Amberlyst-35 was much higher than that on Al-SC and Zn-SC but its EMF selectivity was still lower. This phenomenon was probably due to the synergic effect of active sites such as Zn and Al species, $-\text{SO}_3\text{H}$, phenolic $-\text{OH}$ and $-\text{COOH}$ groups on SC while commercial Amberlyst-35 had only sulfonic site. Table 1 shows the

comparison of glucose transformation into EMF product between our ultrasound-assisted novel systems with previous studies. As obtained, higher EMF yield was clearly obtained while much shorter reaction time and lower reaction temperature were also found in ultrasonic system, resulting in the suppression of humins formation from polymerization. As well known that for conventional thermal system, high reaction temperature ($> 150\text{ }^\circ\text{C}$) was generally required with endothermic nature while it also resulted for facile formation of humins via polymerization reaction, leading to the reduction of EMF yield. Here, the effect of ultrasonic application could be described as follows, for example, (I) it may be correlated with the number of cavitation bubbles and hot spots formed in the medium, and therefore, promoting the fast reaction for EMF formation and (II) it could improve in assisting of the niche collapse which resulted in reduced energy transfer into the reaction system. This also indicates that Al-SC and Zn-SC could be considered as a promising efficient catalyst for ultrasound-assisted glucose conversion to EMF with high yield. It should be noted that the application of Ni-SC was not suitable since low selectivity for EMF production was obtained, resulting from its low acidity. The possible reaction mechanisms for production of EMF and other products from glucose transformation by using acid catalyst are summarized in Fig. 3. Firstly, Lewis acid site of catalyst was required for glucose transformation into fructose. Then, it was further interacted with Brönsted acid site in order to convert the fructose into HMF. At the same time, HMF might be activated by strong Brönsted acid sites of catalyst and followed by ethanol molecule in order to form EMF product (as wanted product) and water. Here, higher acidity is more beneficial for the conversion of glucose via isomerization-dehydration-etherification. In addition, too high acidity also resulted in the facile formation of EL and humins or polymers. Here, the energy and hot spot generated from ultrasonic via cavitation process could well promote the mass transfer process on the substrate towards very fast reaction rate.

In order to access the possibility of as-prepared catalyst for further application in practical processes, the reusability of Al-SC and Zn-SC were also investigated based on turnover rate (TOR) of glucose to EMF. Here, TOR (min^{-1}) obtained by dividing the glucose moles that was converted to EMF per unit catalyst amount and reaction time ($\text{mol/g}\cdot\text{min}$) by catalyst acidity (mol/g). Also, in order to eliminate the factor of varied reactant concentrations due to different activities of the catalysts, the obtained results were performed at the same conversion of glucose (50%). As shown in Fig. 4A, the Zn-SC showed excellent long-term stability and reusability for 4 cycles with small decreasing of EMF yield. Thereafter, the EMF yield was slightly decreased to some extent. This phenomenon could be explained by slight deactivation of catalyst occurred from leaching of sulfonic and Zn species on catalyst surface as

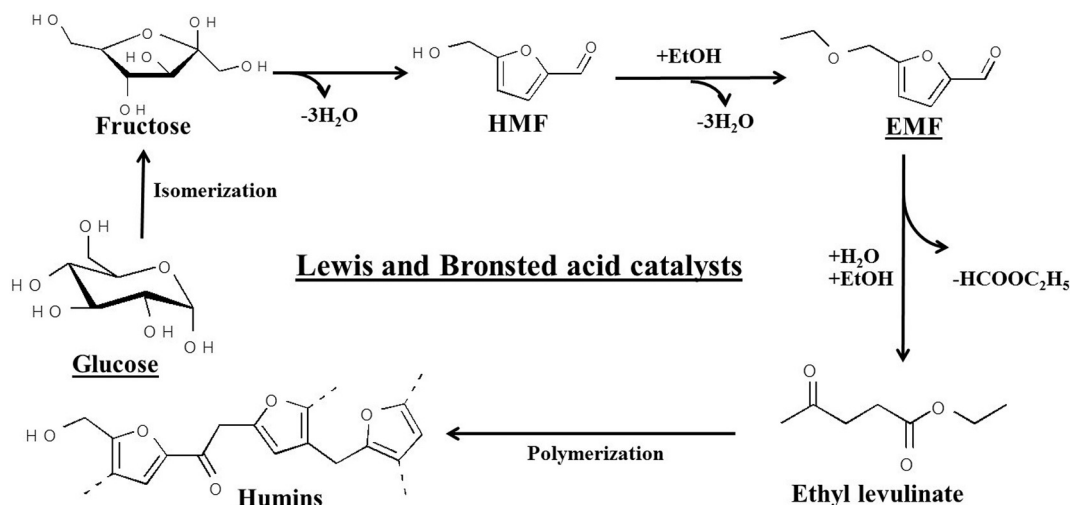


Fig. 3. Possible reaction pathways on conversion of glucose into EMF and other products catalyzed by acid catalyst.

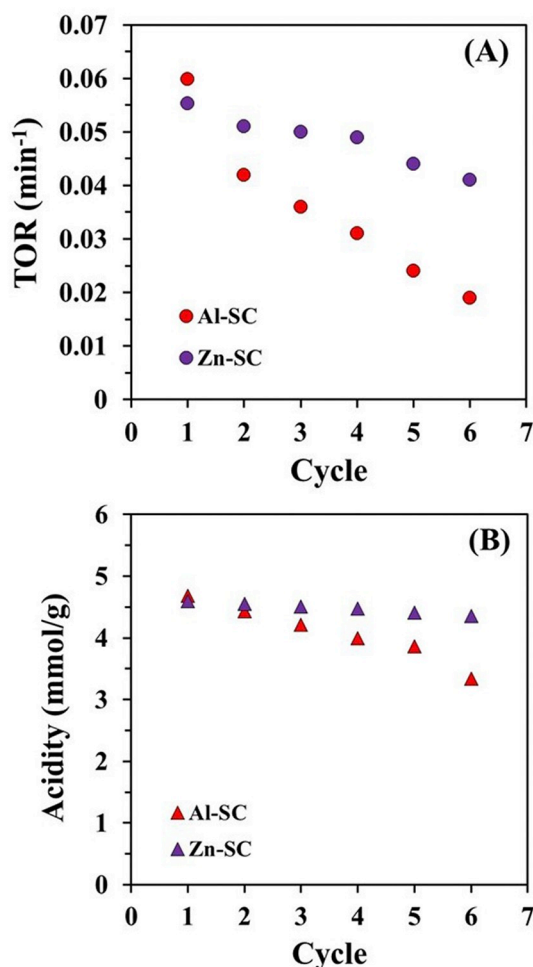


Fig. 4. Recyclability obtained from (A) TOR values and (B) acidities of Al-SC, Zn-SC in each cycle.

well as partial blocking of the catalyst pores by some adsorbed reactants, which inhibited the entrance of glucose and/or intermediate molecules into the active sites [23,24]. The reusability of Al-SC was lower when compared with Zn-SC. This phenomenon should be explained on the different of acid sites. Here, higher amount of strong/Brönsted acid sites of Al-SC based on NH₃-TPD results might promote the formation of site products such as EL and humins. It is possible that leaching amounts of acid and metal species of Al-SC were higher than when compared with Zn-SC. These assumption were supported in Fig. 4B and Table S1. Here, Zn was strongly attached on catalyst structure since very small leaching of Zn amount was found in this study, probably due to strong adsorption interaction between Zn with support. Based on above results, Zn-SC could be possibly applied as a promising green catalyst for EMF production from glucose conversion with contribution of ultrasonic system in practical process.

4. Conclusions

The EMF production from ultrasonic-assisted glucose conversion in biphasic reaction system was achieved over metal-SC. As expected, better catalytic performances were found for Al-SC and Zn-SC when compared with Ni-SC and commercial catalysts. 84.4% and 85.1% of EMF selectivity were achieved by using Al-SC and Zn-SC, respectively. Zn-SC presented the excellent reusability and long-term stability for 6 cycle. The contribution of Brönsted-Lewis acid sites with ultrasound was important for isomerization-dehydration-etherification of glucose. It is expected that our reaction system could be further applied for fast production of EMF in practical process.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.catcom.2019.105767>.

References

- [1] H. Wang, T. Deng, Y. Wang, Y. Qi, X. Hou, Y. Zhu, *Bioresour. Technol.* 136 (2013) 394–400.
- [2] L. Jiang, L. Zhou, J. Chao, H. Zhao, T. Lu, Y. Su, X. Yang, J. Xu, *Appl. Catal. B* 220 (2018) 589–596.
- [3] H. Li, S. Saravanamurugan, S. Yang, A. Riisager, *Green Chem.* 18 (2016) 726–734.
- [4] F.N.D.C. Gomes, F.M.T. Mendes, M.M.V.M. Souza, *Catal. Today* 279 (2017) 296–304.
- [5] P. Wataniyakul, P. Boonnoun, A.T. Quitain, M. Sasaki, T. Kida, N. Laosiripojana, A. Shotipruk, *Catal. Commun.* 104 (2018) 41–47.
- [6] G. Sampath, S. Kannan, *Catal. Commun.* 37 (2013) 41–44.
- [7] M. Zuo, K. Le, Y. Feng, C. Xiong, Z. Li, X. Zeng, X. Tang, Y. Sun, L. Lin, *Ind. Crop. Prod.* 112 (2018) 18–23.
- [8] Y. Yang, M.M. Abu-Omar, C. Hu, *Appl. Energy* 99 (2012) 80–84.
- [9] G.A. Kraus, T. Guney, *Green Chem.* 14 (2012) 1593–1596.
- [10] H. Guo, X. Qi, Y. Hiraga, T.M. Aida, R.L.S. Jr, *Chem. Eng. J.* 314 (2017) 508–514.
- [11] B. Liu, Z. Zhang, K. Huang, Z. Fang, *Fuel* 113 (2013) 625–631.
- [12] X. Zhang, Y. Zhao, Q. Yang, *J. Catal.* 320 (2014) 180–188.
- [13] Y. Liu, H. Li, J. He, W. Zhao, T. Yang, S. Yang, *Catal. Commun.* 93 (2017) 20–24.
- [14] M. Shaikh, S.K. Singh, S. Khilari, M. Sahu, K.V.S. Ranganath, *Catal. Commun.* 106 (2018) 64–67.
- [15] A. Liu, Z. Zhang, Z. Fang, B. Liu, K. Huang, *J. Ind. Eng. Chem.* 20 (2014) 1977–1984.
- [16] X. Liu, H. Li, H. Pan, H. Zhang, S. Huang, K. Yang, W. Xue, S. Yang, *J. Energy Chem.* 25 (2016) 523–530.
- [17] G. Morales, M. Paniagua, J.A. Melero, J. Iglesias, *Catal. Today* 279 (2017) 305–316.
- [18] R.S. Thombal, V.H. Jadhav, *Appl. Catal. A* 499 (2015) 213–216.
- [19] S. Karnjanakom, P. Maneechakr, C. Samart, G. Guan, *Energy Convers. Manag.* 173 (2018) 262–270.
- [20] D. Song, Y. Sun, Q. Zhang, P. Zhang, Y. Guo, J. Leng, *Appl. Catal. A* 546 (2017) 36–46.
- [21] J. Zhao, C. Zhou, C. He, Y. Dai, X. Jia, Y. Yang, *Catal. Today* 264 (2016) 123–130.
- [22] J. Wang, W. Xu, J. Ren, X. Liu, G. Lu, Y. Wang, *Green Chem.* 13 (2011) 2678–2681.
- [23] L. Hu, X. Tang, Z. Wu, L. Lin, J. Xu, N. Xu, B. Dai, *Chem. Eng. J.* 263 (2015) 299–308.
- [24] J.A. Melero, G. Morales, J. Iglesias, M. Paniagua, B. Hernández, S. Penedo, *Appl. Catal. A* 466 (2013) 116–122.
- [25] J. Wang, Z. Zhang, S. Jin, X. Shen, *Fuel* 192 (2017) 102–107.