

## Production of 5-hydroxymethylfurfural from carbohydrates in a biphasic system

ZHAO Yan, LIU Yin, ZHU Jinbo

(School of Materials Science and Engineering, Anhui University of Science and Technology, Huainan 232001, China)

**Abstract:** Cheap catalyst aluminum silicate was combined with HCl to efficiently convert carbohydrates to 5-hydroxymethylfurfural (HMF) in a biphasic system. Glucose can yield 61.5% of 5-HMF in an H<sub>2</sub>O/*n*-butanol biphasic system at 453 K within 30 min. Polysaccharides (sucrose, maltose, starch and cellulose) can also be converted to HMF effectively in this biphasic system at 453 K for 40 min. In addition, aluminum silicate can be reused over five cycles without a significant decrease in its activity. Such catalytic system has the potential to become an efficient and cost-effective approach to the conversion of carbohydrates into bio-fuels and platform chemicals.

**Key words:** biomass; 5-hydroxymethylfurfural; biphasic system; aluminum silicate; glucose

**CLC number:** O636.2      **Document code:** A      doi:10.3969/j.issn.0253-2778.2019.04.003

**Citation:** ZHAO Yan, LIU Yin, ZHU Jinbo. Production of 5-hydroxymethylfurfural from carbohydrates in a biphasic system[J]. Journal of University of Science and Technology of China, 2019, 49(4):276-281.  
赵岩,刘银,朱金波. 双相体系中催化碳水化合物水解制备 5-羟甲基糠醛[J]. 中国科学技术大学学报, 2019, 49(4):276-281.

## 双相体系中催化碳水化合物水解制备 5-羟甲基糠醛

赵岩,刘银,朱金波

(安徽理工大学材料科学与工程学院,安徽淮南 232001)

**摘要:** 采用廉价催化剂硅酸铝盐与痕量的盐酸组合,在双相体系中催化碳水化合物有效地转化制备 5-羟甲基糠醛(HMF)。葡萄糖在水/正丁醇两相体系中在 453 K 下反应 30min 达到了 100%的转化率,并可以获得 61.5%产率的 HMF。同时,在双相体系中在 453 K 下反应 40min 能有效地转化多糖(蔗糖、麦芽糖、淀粉和纤维素)制备 HMF。此外,硅酸铝盐可以多次重复使用,试验中重复 5 次以上其活性没有明显下降。本催化体系在碳水化合物转化制备生物燃料和化学品领域具有很好的成本效益和商业应用潜力。

**关键词:** 生物质; 5-HMF; 双相; 硅酸铝; 葡萄糖

### 0 Introduction

With the depletion of fossil resources and the

increase in energy demand, more and more people are transferring to fields related to the development and utilization of sustainable

**Received:** 2017-12-19; **Revised:** 2018-11-06

**Foundation item:** Supported by Anhui Natural Science Foundation (1808085QB54), China Postdoctoral Science Foundation (2017M621989), Anhui Province Postdoctoral Science Foundation(2017B216).

**Biography:** ZHAO Yan(corresponding author), male, born in 1985, PhD. Research field:biomass resources, E-mail:yanz@mail.ustc.edu.cn

resources<sup>[1]</sup>. Biomass is one of the most abundant renewable resources and has attracted much more attention to the substitution of the petroleum resource to obtain fuels and chemicals<sup>[2-4]</sup>. 5-hydroxymethylfurfural (HMF) is an important platform molecule and a precursor of liquid fuels. It can be obtained from biomass-based carbohydrates<sup>[5-8]</sup>. However, the high cost of production of 5-HMF has hampered its industrial production<sup>[9]</sup>.

Glucose is the most abundant and cheapest monosaccharide in nature<sup>[10]</sup>. It would be very beneficial to generate valuable compounds from glucose<sup>[11]</sup>. However, obtaining HMF from glucose is much more difficult than from fructose, which can be attributed to the stable ring structure<sup>[12]</sup>.

It has been proposed that conversion of glucose to HMF can occur via isomerization of glucose to fructose and subsequent dehydration of fructose<sup>[13-17]</sup>. Zhao et al<sup>[18]</sup> have demonstrated that glucose could be converted into HMF in 67% yield using  $\text{CrCl}_2$  in 1-ethyl-3-methylimidazolium chloride ( $[\text{EMIM}]\text{Cl}$ ).  $\text{SnCl}_4$  in ionic liquids has also been proven very effective in converting glucose to HMF. A maximum HMF yield of 64% was obtained at 373 K for 3 h in 1-ethyl-3-methylimidazolium tetrafluoroborate ( $[\text{EMIM}]\text{BF}_4$ )<sup>[19]</sup>. However, these metal chlorides are toxic, and ionic liquids are expensive, so these catalytic systems are not suitable for large-scale production. Carrying out the reaction in an aqueous solution has the lowest efficiency. However, in an aqueous solution the reaction leads to further degradation of HMF to levulinic acid and humins. Biphasic systems combining with water and a water-immiscible organic solvent, can not only prevent the degradation and aggregation of HMF, but also facilitate the separation and purification of the product. The yield of HMF 39.7% in a biphasic system ( $\text{H}_2\text{O}$ /tetrahydrofuran (THF) mixture was used as the solvent) was achieved<sup>[20]</sup>. Although metal chlorides are active Lewis acid catalysts for glucose isomerization, separation and recycling of the catalyst is a challenge. Using Sn-beta and HCl in a biphasic ( $\text{H}_2\text{O}$ /THF) system, 79% glucose conversion and

72% HMF selectivity were obtained at 453 K for 70 min<sup>[21-22]</sup>. However, the complex preparation of Sn-beta made its application prospects blocked. A low cost and efficient conversion of glucose to HMF is still a challenge.

In this paper, the combination of aluminium silicate and HCl was proven to be very effective in the synthesis of HMF from glucose in a  $\text{H}_2\text{O}/n$ -butanol biphasic medium. Aluminium silicate was a cheap and abundant chemical and was used as catalyst. Polysaccharides as raw materials in this system were also studied.

## 1 Experimental

### 1.1 Materials

Sucrose, NaCl, *n*-butanol, 2-butanol, tetrahydrofuran, methyl-isobutyketone (MIBK), starch and hydrochloric acid were purchased from Sinopharm Chemical Reagent Co., Ltd. Glucose, maltose, cellobiose, 2-methyltetrahydrofuran (2-MTHF) and aluminium silicate were purchased from Shanghai Aladdin Reagent Co., Ltd. Cellulose and HMF was purchased from Aldrich. All reagents and solvents were used as supplied without further purification.

### 1.2 Characterization

BET surface area and pore volumes of samples were determined by  $\text{N}_2$  physisorption technique on Micromeritics ASAP 2000 adsorption analyzer. The X-ray diffraction (XRD) patterns of powder were conducted on Panalytical X'Pert PRO X-ray diffractometer using Cu  $K\alpha$  radiation.  $\text{CO}_2$ -TPD (temperature programmed desorption) was applied to characterize the alkaline sites of aluminium silicate on Micromeritics ChemiSorb 2750 chemisorb analyzer. In detail, aluminium silicate (0.1 g) was treated at 823 K in argon for 1 h and then purged with  $\text{CO}_2$  in a pulse way for 90 min after cooling to 353 K. The sample was purged further with Ar at 30 mL/min for 60 min, and then was heated to 973 K at 10 K/min under argon.

### 1.3 Reaction testing

In a typical experiment, 0.5 g of carbohydrates, 1.75 g of NaCl, 0.125 g of aluminium silicate, 5 mL of pH=1 HCl aqueous solution and 15 mL of organic solvent were added

to a Parr reactor (50 mL). The mixture was heated to the desired temperature in less than 35 min with vigorous stirring. After the reaction was completed, the parr reactor was quickly quenched in a cool water bath. In the reuse experiment of catalyst, aluminium silicate was collected and washed for 3 times with acetone and dried in 353 K for 24 h for the next use.

#### 1.4 Analysis methods

Quantitative analyses of glucose and fructose were performed by high performance liquid chromatography (HPLC) using a Waters 1525 pump, a Nacalai Tesque cosmail Paked Sugar-D column and a Waters 2414 refractive index detector. Acetonitrile and water (3 : 1 v/v) were used as the mobile phase at 303 K with a flow rate of 1.0 mL/min. HMF was quantified by HPLC equipped with a Nacalai Tesque cosmail 5C18-AR-II column and Hitachi L-2000 HPLC system. The mobile phase was water and methanol (9 : 1 v/v) at 303 K with a flow rate of 1.0 mL/min.

## 2 Results and discussion

### 2.1 Characterization of the catalyst

Brunauer-Emmett-Teller (BET) isotherms of  $N_2$  adsorption showed that the BET surface area of aluminium silicate was  $78.98 \text{ m}^2/\text{g}$  and the pore volume was  $0.38 \text{ cm}^3/\text{g}$ . In the XRD patterns of aluminium silicate before and after reactions, the amorphous peaks can be found (Fig. 1 (a)). However, the crystal diffraction peaks can not be observed in the range of  $5^\circ \sim 70^\circ$ , which indicates that aluminum silicate is not a crystal structure. The  $\text{CO}_2$ -TPD profiles for aluminum silicate is shown in Fig. 1(b). A peak can be observed on  $\text{CO}_2$ -TPD profile, indicating the presence of base sites on the surface. Isomerization of glucose may be attributed to the basic sites<sup>[23-24]</sup>.

### 2.2 Contrast experiments

Tab. 1 shows that the various components in the reaction system have an important influence on the reaction. In a single phase and a biphasic system, aluminium silicate and HCl were combined and tested for their activity towards conversion of glucose to HMF. Entries 1 and 2 in Tab. 1 clearly show that in the biphasic system both glucose conversion and HMF yield are higher than those in

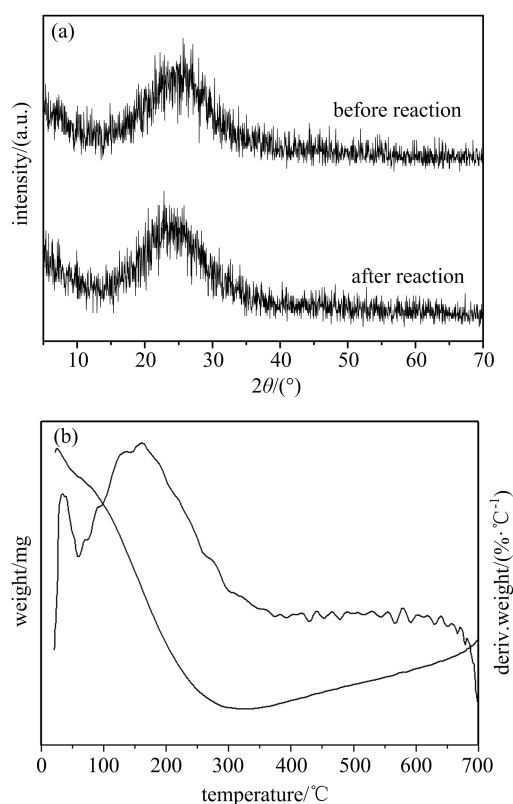


Fig. 1 (a) The XRD patterns of aluminium silicate before and after reactions, (b) the  $\text{CO}_2$ -TPD profiles for aluminium silicate

the single-phase system under the same conditions. These results could be attributed to the timely extraction of HMF by *n*-butanol from the aqueous phase in order to avoid the degradation and aggregation of HMF under aqueous acidic conditions. In an  $\text{H}_2\text{O}/n$ -butanol biphasic system with HCl as catalytic system, the conversion of glucose was 29.5% and the yield of HMF was 12.5% at 433 K for 90 min. When aluminum silicate replaced HCl as a catalyst under the same conditions, the conversion of glucose increased to 49.5% while the yield of HMF was only 11.5%. However, the combination of aluminum silicate with HCl resulted in both higher glucose conversion and HMF yield than either HCl or aluminum silicate used as catalyst (Tab. 1, entries 3, 4 and 5). The result of  $\text{CO}_2$ -TPD has confirmed the existence of the basic sites on the aluminum silicate. So this result might be attributed to the basic sites existing on aluminum silicate via isomerization reaction of glucose to fructose, while HCl could be efficiently implemented fructose dehydration to HMF. Furthermore, NaCl has been proven to effectively improve the selectivity

of HMF, making it an integral component in the  $H_2O/n$ -butanol biphasic system (Tab. 1, entries 2 and 5). These results are consistent with previous reports, showing that the addition of NaCl to the aqueous phase increases the partitioning of HMF into the organic phase, thus restraining the degradation of HMF into byproducts under aqueous acidic conditions<sup>[25]</sup>.

Tab. 1 Results of conversion of glucose to HMF

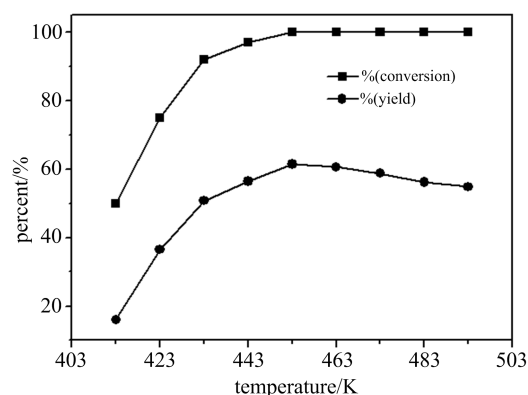
entry	system	catalyst	conversion	yield/%
1	single phase( $H_2O$ )	aluminium silicate, HCl	65.5	13
2	biphasic ( $H_2O/1$ -butanol)	aluminium silicate, HCl	100	29
3	biphasic( $H_2O/1$ -butanol/NaCl)	HCl	29.5	12.5
4	biphasic( $H_2O/1$ -butanol/NaCl)	aluminium silicate	49.5	11.5
5	biphasic( $H_2O/1$ -butanol/NaCl)	aluminium silicate, HCl	100	47.5

[Note]Reaction condition: HCl: 5 mL, pH=1; aluminium silicate: 0.125 g; glucose: 0.5 g; NaCl: 1.75 g;  $n$ -butanol: 15 mL; reaction temperature: 433 K; reaction time: 90 min.

### 2.3 Effect of reaction temperature and reaction time on the glucose conversion to HMF

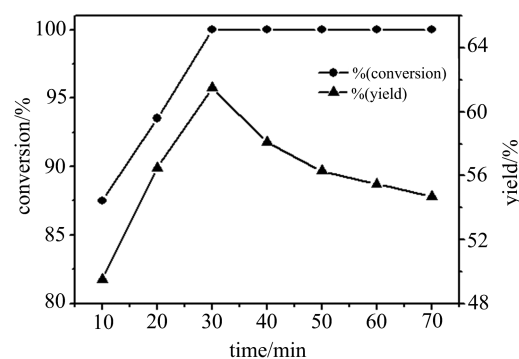
Fig. 2 shows the effect of reaction temperature on the glucose conversion and the HMF yield in the  $H_2O/n$ -butanol biphasic system. The conversion of glucose increased from 50% (413 K) to 100% (453 K), and the yield of HMF was also increased to 61.5% at 453 K for 30 min. However, when the temperature was further raised, the conversion of glucose was maintained at 100%, while the yield of HMF decreased slightly. It is assumed that the decrease of HMF yield at higher temperatures could be due to the formation of undesired byproducts, such as humins and cokes<sup>[26]</sup>.

The effect of reaction time on the glucose conversion and the HMF yield at 453 K is shown in Fig. 3. It was confirmed that aluminum silicate combined with HCl is highly active for the dehydration of glucose to HMF, since the conversion of glucose could mount to 100% and HMF yield could also reach 61.5% at 453 K for 30 min. Further increasing the reaction time led to a decrease in the yield of HMF. This could also be attributed to the formation of byproducts



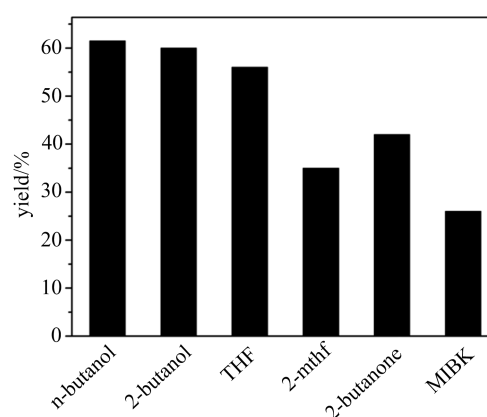
Reaction condition: HCl: 5 mL, pH = 1; aluminium silicate: 0.125 g; glucose: 0.5 g; NaCl: 1.75 g;  $n$ -butanol: 15 mL; reaction time: 30 min

Fig. 2 The effect of temperature on the glucose conversion and HMF yield



Reaction condition: HCl: 5 mL, pH = 1; aluminium silicate: 0.125 g; glucose: 0.5 g; NaCl: 1.75 g;  $n$ -butanol: 15 mL; reaction temperature: 453 K.

Fig. 3 The effect of time on the glucose conversion and HMF yield



Reaction condition: HCl: 5 mL, pH = 1; aluminium silicate: 0.125 g; glucose: 0.5 g; NaCl: 1.75 g;  $n$ -butanol: 15 mL; reaction time: 30 min; reaction temperature: 453 K.

Fig. 4 The effect of organic solvents on the HMF yield

(Levulinic acid etc.) with the long reaction time.

### 2.4 Effect of different organic solvents on HMF yield

The effect of different organic solvents on the

dehydration reaction of glucose to HMF in a biphasic system was also studied (Fig. 4). In a biphasic system with different organic solvents the glucose was completely converted, but the HMF yield was quite different at 453 K for 30 min. The highest HMF yield (61.5%) was achieved using *n*-butanol as an extracting solvent at 453 K for 30 min. When 2-butanol or THF replaces *n*-butanol as organic phase, the yield of HMF could also reach 60% or 56% under the same conditions. 2-butanone as an extracting solvent was also studied, and the yield of HMF was 42% in an H<sub>2</sub>O/2-butanone biphasic system. However, when 2-MTHF or MIBK was used as an aqueous phase, HMF yield was 35% or 26%, respectively. Low HMF yield could be attributed to side reactions which had not been effectively suppressed, since a lot of coke and humins could be observed after the reaction.

### 2.5 Production of HMF from complex carbohydrates

Disaccharides (maltose, cellobiose and sucrose) and polysaccharides (starch and cellulose) as substrates were also investigated in an H<sub>2</sub>O/*n*-butanol biphasic system. In order to confirm the complete conversion of these disaccharides and starch, the reaction time was extended to 40 min. The HMF yield from sucrose was the highest, since sucrose contained one fructose molecule per unit (Tab. 2, entry 1). Conversion of cellobiose and starch to HMF was comparable to that of maltose (Tab. 2, entries 2~4). These results show that aluminum silicate coupled with HCl could be used for conversion of disaccharides and starch to HMF. However, when cellulose was used as the substrate, part of the cellulose remained unconverted and HMF yield was only 23% even at 473 K for 40 min. The poor reactivity with cellulose might be due to its recalcitrant structure<sup>[27]</sup>. More severe conditions may be needed to promote the conversion of cellulose.

### 2.6 Catalyst recycling

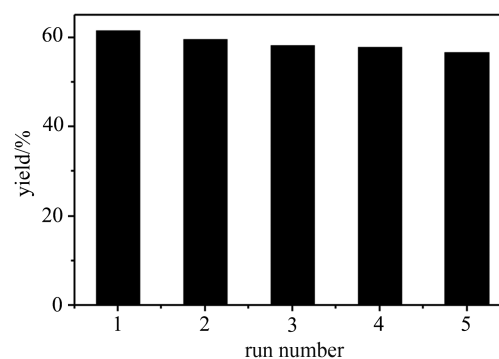
To test the catalyst stability, aluminum silicate was repeatedly used several times in an H<sub>2</sub>O/2-butanol biphasic system. The results show that aluminum silicate activity did not decrease significantly

and the yield of HMF was still 57% after five cycles in this system (Fig. 5). Therefore, aluminum silicate can be separated and reused.

**Tab. 2 Conversion of the complex carbohydrates into HMF**

entry	feed	yield/%	time/min	temperature/K
1	sucrose	56.5	40	453
2	maltose	50	40	453
3	cellobiose	49	40	453
4	starch	50	40	453
5	cellulose	23	40	473

[Note] Reaction condition: HCl: 5 mL, pH = 1; aluminium silicate: 0.125 g; carbohydrates: 0.5 g; NaCl: 1.75 g; *n*-butanol: 15 mL.



**Fig. 5 Reuse of aluminium silicate**

## 3 Conclusion

This paper presented an efficient route of converting glucose into HMF catalyzed by aluminum silicate coupled with HCl. The yield of HMF (61.5%) was obtained in an H<sub>2</sub>O/*n*-butanol biphasic system at 453 K for 30 min. Some complex carbohydrates could be efficiently converted into HMF. Additionally, aluminum silicate could be reused over five cycles and its activity did not decrease significantly. In a word, this catalytic system has the potential of producing HMF at a lower cost.

### References

- [1] YANG F, LIU Q, YUE M, et al. Tantalum compounds as heterogeneous catalysts for saccharide dehydration to 5-hydroxymethylfurfural[J]. *Chemical Communications*, 2011, 47(15): 4469-4471.
- [2] MA H, LONG J X, WANG F R, et al. Conversion of cellulose to butyl levulinate in bio-butanol medium catalyzed by acidic ionic liquids[J]. *Acta Physico-Chimica Sinica*, 2015, 31(5): 973-979.
- [3] ZHANG Z, ZHAO Z K. Production of 5-

- hydroxymethylfurfural from glucose catalyzed by hydroxyapatite supported chromium chloride [J]. *Bioresource Technology*, 2011, 102(4): 3970-3972.
- [4] XU L, ZHANG Y, FU Y. Advances in upgrading lignin pyrolysis vapors by ex situ catalytic fast pyrolysis[J]. *Energy Technology*, 2017, 5(1): 30-51.
- [5] GONG Y Y, LIU M, JIA S Y, et al. Production of 5-hydroxymethylfurfural from inulin catalyzed by sulfonated amorphous carbon in an ionic liquid[J]. *Acta Physico-Chimica Sinica*, 2012, 28(3): 686-692.
- [6] CHE P, LU F, ZHANG J, et al. Catalytic selective etherification of hydroxyl groups in 5-hydroxymethylfurfural over  $H_4SiW_{12}O_{40}/MCM-41$  nanospheres for liquid fuel production[J]. *Bioresource Technology*, 2012, 119: 433-436.
- [7] PAWAR H S, LALI A M. Polyvinyl alcohol functionalized solid acid catalyst DICAT-1 for microwave-assisted synthesis of 5-hydroxymethylfurfural in green solvent[J]. *Energy Technology*, 2016, 4(7): 823-834.
- [8] SHEN Y, ZHANG Y, CHENY, et al. Combination of Brønsted and Lewis polymeric catalysts for efficient conversion of cellulose into 5-hydroxymethylfurfural (HMF) in ionic liquids[J]. *Energy Technology*, 2016, 4(5): 600-609.
- [9] ROMÁN-LESHKOV Y, CHHEDA J N, DUMESIC J A. Phase modifiers promote efficient production of hydroxymethylfurfural from fructose [J]. *Science*, 2006, 312(5782): 1933-1937.
- [10] YANG Y, HU C, ABU-OMARM M. Conversion of glucose into furans in the presence of  $AlCl_3$  in an ethanol-water solvent system [J]. *Bioresource Technology*, 2012, 116: 190-194.
- [11] QI X, WATANABE M, AIDAT M, et al. Synergistic conversion of glucose into 5-hydroxymethylfurfural in ionic liquid-water mixtures [J]. *Bioresource Technology*, 2012, 109: 224-228.
- [12] ZAKRZEWSKA M E, BOGEL-ŁUKASIK E, BOGEL-ŁUKASIKR. Ionic liquid-mediated formation of 5-hydroxymethylfurfural: A promising biomass-derived building block[J]. *Chemical Reviews*, 2010, 111(2): 397-417.
- [13] YANG Y, HU C, ABU-OMARM M. Conversion of carbohydrates and lignocellulosic biomass into 5-hydroxymethylfurfural using  $AlCl_3 \cdot 6H_2O$  catalyst in a biphasic solvent system[J]. *Green Chemistry*, 2012, 14(2): 509-513.
- [14] VAN PUTTEN R J, VAN DER WAAL J C, DE JONG E D, et al. Hydroxymethylfurfural, a versatile platform chemical made from renewable resources[J]. *Chemical Reviews*, 2013, 113(3): 1499-1597.
- [15] BERMEJO-DEVAL R, ORAZOV M, GOUNDER R, et al. Active sites in Sn-Beta for glucose isomerization to fructose and epimerization to mannose[J]. *ACS Catalysis*, 2014, 4(7): 2288-2297.
- [16] CHOUDHARY V, MUSHRIF S H, HO C, et al. Insights into the interplay of Lewis and Brønsted acid catalysts in glucose and fructose conversion to 5-(hydroxymethyl) furfural and levulinic acid in aqueous media[J]. *Journal of the American Chemical Society*, 2013, 135(10): 3997-4006.
- [17] FENG Y, LI M, GAO Z, et al. Development of betaine-based sustainable catalysts for green conversion of carbohydrates and biomass into 5-hydroxymethylfurfural [J]. *ChemSusChem*, 2019, 12(2): 495-502.
- [18] ZHAO H, HOLLADAY J E, BROWNH, et al. Metal chlorides in ionic liquid solvents convert sugars to 5-hydroxymethylfurfural [J]. *Science*, 2007, 316(5831): 1597-1600.
- [19] HU S, ZHANG Z, SONG J, et al. Efficient conversion of glucose into 5-hydroxymethylfurfural catalyzed by a common Lewis acid  $SnCl_4$  in an ionic liquid [J]. *Green Chemistry*, 2009, 11(11): 1746-1749.
- [20] SHEN Y, SUN J, YI Y, et al.  $InCl_3$ -catalyzed conversion of carbohydrates into 5-hydroxymethylfurfural in biphasic system [J]. *Bioresource Technology*, 2014, 172: 457-460.
- [21] NIKOLLA E, ROMÁN-LESHKOV Y, MOLINERM, et al. "One-pot" synthesis of 5-(hydroxymethyl) furfural from carbohydrates using tin-beta zeolite [J]. *ACS Catalysis*, 2011, 1(4): 408-410.
- [22] TAKAGAKI A, OHARA M, NISHIMURA S, et al. A one-pot reaction for biorefinery: Combination of solid acid and base catalysts for direct production of 5-hydroxymethylfurfural from saccharides[J]. *Chemical Communications*, 2009(41): 6276-6278.
- [23] DESPAX S, ESTRINE B, HOFFMANN, et al. Isomerization of D-glucose into D-fructose with a heterogeneous catalyst in organic solvents [J]. *Catalysis Communications*, 2013, 39: 35-38.
- [24] SOUZA R O L, FABIANO D P, FECHE C, et al. Glucose-fructose isomerisation promoted by basic hybrid catalysts[J]. *Catalysis Today*, 2012, 195(1): 114-119.
- [25] ROMÁN-LESHKOV Y, DUMESIC J A. Solvent effects on fructose dehydration to 5-hydroxymethylfurfural in biphasic systems saturated with inorganic salts[J]. *Topics in Catalysis*, 2009, 52(3): 297-303.
- [26] TSILOMELEKIS G, ORELLA M J, LIN Z, et al. Molecular structure, morphology and growth mechanisms and rates of 5-hydroxymethyl furfural (HMF) derived humins[J]. *Green Chemistry*, 2016, 18(7): 1983-1993.
- [27] TAO F, SONG H, CHOUL. Hydrolysis of cellulose in  $SO_3H$ -functionalized ionic liquids[J]. *Bioresource Technology*, 2011, 102(19): 9000-9006.