One Step Conversion of Glucose into 5-Hydroxymethylfurfural (HMF) via a Basic Catalyst in Mixed Solvent Systems of Ionic Liquid-Dimethyl Sulfoxide

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Abstract: A simple solid base catalyst, ammonium aluminum carbonate hydroxide (AACH), was prepared and its structure was characterized by many technologies, including XRD, FT-IR, SEM, BET and Elemental Analysis. The prepared catalyst was used to catalyze the conversion of glucose into 5-hydroxymethylfurfural (HMF) in ionic liquid 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]) and dimethyl sulfoxide (DMSO) mixtures. Various reaction conditions, including catalyst loading, reaction temperature, reaction duration and solvent, were investigated. A moderated HMF yield of 52.17 % was obtained at the mild reaction conditions (120°C for 4 h). More importantly, the catalyst could be reused for several times without the loss of its significant catalytic activities. After five reaction runs, a HMF yield about 49.34 % was also obtained.

Key words: HMF, glucose, heterogeneous catalysis, ionic liquid

1 Introduction

5-hydroxymethylfurfural (HMF) is an important and versatile biomass-based platform chemical, which can be further converted into a wide variety of fine chemicals, polymeric materials, pharmaceuticals and liquid fuels[1-4]. Nowadays, the works of HMF converted from carbohydrates, such as glucose and fructose, are hot and significant both in science and commerce[5, 6]. Among these carbohydrates, fructose was proved easily converted into HMF[7]. However, the practical production of HMF from fructose is very limited because of its low availability and high price. In constrast, glucose, another improtant hexose with a lower price and vaster availability, has been considered as a preferred raw materials to produce HMF. But unfortunately, glucose is hard to be transformed into HMF because of its stable six-membered pyranoside structure[8-10]. Hence, it is nessesary to find a proper catalyst to degrade glucose into HMF.

From many pervious works[11-13], it was known that the reaction process on the conversion of glucose into HMF contained two steps. Firstly, glucose was isomerized into fructose; Secondly, fructose was dehydrated into HMF. In the two steps, the isomerization process was the hard and control step. The dehydration process was the easy and fast step. The results indicated that the high-performance catalyst on the conversion of glucose into HMF should own high isomerization capacity. At present, various acid catalysts, including homogeneous and heterogeneous catalysts, were employed to produce HMF from glucose and have been always the major catalyst for the conversion of glucose into HMF. For instance, the homomgenous acid catalysts, such as metal salts, ionic liquid, mineral acid, inorganic and organic acid[14-18], and the heterogeneous acid actalysts, such as zeolites, Al2O3-based catalysts, Nb-based catalysts, carbon-based catalysts, polymer-based catalysts and phosphate-based catalysts[19-28], have been applied to synthesis of HMF from glucose. Other typological catalysts has been few reported. However just because of their acidity of acid catalysts, a number of side reactions will be happened in the process of production of HMF from glucose. The Bronsted acid sites[29-31] will possibly cause the target product HMF decomposed or reacted with other products such as gulcose, fructose into small or large molecular compounds, such as fromic acid, levulinic acid, humins. The Lewis acid sites[32-34] will possibly arouse glucose isomerized into other monosaccharides rather than fructose like galactose, mannose, and possibly reacted with themselves, other monosaccharides or HMF into macromo-
lucar compounds like humins. All the results bring the decrease of yield and selectivity of HMF and restrict the development of the production of HMF from glucose under the acid catalysts. Therefore, it is necessary to develop other typical catalyst to synthesis of HMF from glucose.

Recently, it is found that the increase of the alkalinity of catalyst or catalytic system would effectively improve the isomerization ability of glucose into fructose. For instance, Deng et al.\(^{38}\) proved using the alkali oxides SnOx, CeOx to modify the catalyst Ni/Al\(_2\)O\(_3\) can significantly improve the isomerization ability of the catalyst Ni/Al\(_2\)O\(_3\). Irretratonyena et al.\(^{39}\) demonstrated that after impregnation of alkali oxide MgO in the surface of NaY, its isomerization ability of glucose into fructose increased significantly, selectivities of fructose were up to 66-96% according to the loading capacity from 0-15\%. Meng et al.\(^{40}\) used base compound MnSn(OH)\(_4\) as frist catalyst to improve glucose isomerized into fructose and acid resin Amberlyst-15 as second catalyst to improve fructose dehydrated into HMF, and ca.53% yield and 70% selectivity of HMF were obtained. Sampath et al.\(^{41}\) also found addition of metal salt (CuCl\(_2\), CaCl\(_2\)) into alumina catalytic system can significantly increased the isomerization of glucose into fructose and HMF yield. Furthermore, in the past few years, Zhang et al.\(^{42}\) also discovered that after adding the alkali compound NaN\(_3\)-dimethylacetamide (DMAC) into CrCl\(_3\)/[Bnim][Cl] catalytic system, HMF yield has a remarkable increase from 62.5\% into 81\%. However, there has been not reports of production of HMF from glucose via one-step solid base catalyst with moderate HMF yield until now, since the performance on the synthesis of HMF from glucose catalyzed only by solid base catalysts was not good, such as NaOH, MgO, CuO, Hydrotrilite and so on, which HMF yields were not more than 35\%.\(^{40}\) Therefore, it is worthwhile to do some researchs to discover a base solid catalyst with well performance on synthesis of HMF from glucose.

Reaction medium is another factor for the conversion of glucose into HMF. Since Zhao\(^{41}\) has reported that the catalytic system with ionic liquid 1-ethyl-3-methylimidazolium as reaction medium has well catalytic activity for the conversion of glucose into HMF with a high HMF yield of 69\%. Many researchers used ionic liquids as reaction mediums or catalysts to produce HMF from monosaccharides. For instance, Qi et al.\(^{42-44}\) used ionic liquids as reaction mediums or catalysts to successfully and highly synthesize HMF from fructose and glucose. Moreau et al.\(^{45}\) successfully applied 1-H-3-methyl imidazolium chloride both as solvent and catalyst to produce HMF from glucose and sucrose. And all those works suggested that the excellent performance of ionic liquid might be ascribed that ionic liquid can suppressed decomposition of HMF because of activation energy of fructose dehydration of HMF is lower in ionic liquids than in organic solvents. The results indicated ionic liquid is a desired reaction medium. However, due to the high viscosity of ionic liquid, reaction materials will be hard to move and contact with catalyst in some reaction systems. The mixed mediums of ionic liquid and other aprotic solvent were developed and excellent HMF yields were obtained, such as ionic liquid/DMAC,\(^{38}\) ionic liquid/ NH\(_4\)Br,\(^{49}\) liquid/DMSO.\(^{50}\) Among those aprotic solvents, DMSO is the common used reaction solvent. Furthermore, some studies\(^{47-50}\) shows that DMSO also can suppressed decomposition of HMF and promote the dehydration of fructose into HMF.

In the work, A simple base catalyst, ammonium aluminum carbonate hydroxide (AACH), was prepared and used to synthesize HMF from glucose under ionic liquid 1-buthyl-3-methylimidazolium chloride ([Bnim][Cl]) and dimethyl sulfoxide (DMSO) mixtures. Various reaction parameters, including reaction durations, reaction temperature, catalytic loading, reaction solvent, were investigated. In addition, the possible catalytic mechanism were also proposed.

2 Experimental

2.1 Materials

Ionic liquid, 1-buthyl-3-methylimidazolium chloride ([Bnim][Cl], AR) was purchased from Shanghai Cheng Jie Chemical Co. Ltd. (Shanghai China). HMF standard sample (AR) was supplied by Aladdin Reagent Co. Ltd. (Shanghai China). All of other reagents were analytic grade, purchased from Sinopharm Chemical Reagent Co. Ltd. and used as received.

2.2 Catalysts preparation

AACH was prepared via the hydrothermal synthetic method. In a typical synthesis, 2 mmol AlCl\(_3\)-6H\(_2\)O and 36 mmol urea were added into 50mL deionized water. Then, the solution was transferred into a 100 mL Tellon-lined stainless autoclave, sealed and then heated at 190\(^\circ\)C for 36 h. Subsequently, the autoclave was cooled to room temperature naturally. The product was collected through centrifugation and washed several times with deionized water. Finally, the AACH sample was obtained by drying the product in a vacuum at 100\(^\circ\)C for 6 h.

2.3 Catalysts characterization

The structures of samples were determined by Panalytical X-ray diffraction (XRD) analysis with Cu-K\(_\alpha\) radiation (\(\lambda =1.5406\) \(\AA\)). The data were recorded over 20 range of 10-80\(^\circ\). The characterizations of functional groups in the samples were detected by Fourier transform infrared spectra (FT-IR, Nexusftir, Nieolet). The textural properties of the samples were detected via nitrogen adsorption-desorption experiments measured by a Micromeritics ASAP 2020 system. The specific surface area and pore size distribution were calculated using Brunauer-Emmett-Teller
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2.4 Typical procedure of HMF from glucose

The catalytic processes were carried out in the tube of 18 mm × 180 mm with a lid. In the typical process, 100 mg (0.56 mmol) glucose and 300 mg (2.15 mmol) AACH were added into 1 g ionic liquid (Bmim) Cl and 1 g DMSO under vigorous stirring to form a homogeneous solution, and then the tube was heated at 120 °C for 4 h under 500 rpm magnetic stirring. Afterwards, the reaction mixture was quickly cooled to room temperature and 20 ml cold deionized water was added into the reaction mixture. The water-added mixtures were centrifuged at 10000 rpm for 5 min. The above clear liquid was collected. After diluted 150-200 times by the deionized water, the solution was sent to be analyzed. It should be warned that all these experiments were carried out at three times in order to check the stability of the catalytic system and got an average results.

2.5 Analysis

HMF was detected by High Performance Liquid Chromatography (HPLC, Agilent 1200) equipped with ultraviolet detector (UV-9600, Beijing Purkinje General Instrument CO. Ltd., China) at the ultraviolet wavelength of 284 nm via External standard method. Glucose and fructose were also checked by High Performance Liquid Chromatography (HPLC, Agilent 1200) equipped with a refractive index with an ion exclusion column (300 mm × 7.8 mm, Aminex HPX-87H) at 60 °C. The condition of mobile phase was 0.0075 M H2SO4 at a flow rate of 0.4 mL min⁻¹. The yield of HMF and conversion of glucose were calculated according to the following equations:

\[
\text{Glucose conversion} = \frac{100\% - \text{mole of glucose in the product}}{\text{mole of starting glucose}} \times 100\%
\]

\[
\text{Fructose yield} = \frac{\text{mole of Fructose}}{\text{mole of starting glucose}} \times 100\%
\]

\[
\text{HMF yield} = \frac{\text{mole of HMF}}{\text{mole of starting glucose}} \times 100\%
\]

3 Results and Discussions

3.1 Catalyst characterization

The product AACH was characterized by XRD and FT-IR. All the results show that AACH was successfully prepared. The XRD pattern of the sample (Fig. 1) shows that all the diffraction peaks are indexed into the orthorhombic AACH, which is in good agreement with JCPDS Card 042-0250. No peaks of other phases are found in the pattern, indicating the high purity of the product AACH. Further evidence for formation of AACH (with formula NH₄Al(OH)₂CO₃) can be supported from the results of its FT-IR (Fig. 2) and chemical composition (Table 1). In Fig. 2, there are four typical peaks of OH, NH₄⁺, CO₃²⁻, AlO₆. The bands at 3443 and 985 cm⁻¹ belong to the ν OH and δ OH vibrations, respectively. The bands at 3175, 3018 and 2840 cm⁻¹ are assigned to ν N-H stretching vibrations, and the bands at 1828 and 1723 cm⁻¹ are indexed to δ N-H stretching vibrations. While, the bands at 1545, 1452 and 1001 cm⁻¹ are assigned to the bending vibrations of H₂O.

Fig. 1 XRD pattern of the AACH.

Fig. 2 FT-IR spectrum of the AACH.
1382 cm\(^{-1}\) belong to \(\nu_3\) vibrations of \(\text{CO}_3^{2-}\), and the bands at 1105, 850 and 760 cm\(^{-1}\) are assigned to \(\nu_1\), \(\nu_2\) and \(\nu_4\) of \(\text{CO}_3^{2-}\) vibrations, respectively. Finally, the three bands at 751, 630, and 484 cm\(^{-1}\) represent the vibration mode of \(\text{AlO}_6\). From the chemical composition of the AACH in Table 1, it can be inferred that the chemical formula of the catalyst was \(\text{NH}_4\text{Al(OH)}_{2.03}\text{CO}_3\), which was very close to the standard \(\text{NH}_4\text{Al(OH)}\text{CO}_3\). The slight difference may be stemmed from the surface adsorption water of the AACH or the experimental error. In brief, all results indicated that AACH was successfully prepared.

The textural property of the AACH was further detected via N\(_2\) adsorption and desorption measurement. In Fig. 3, it can be seen that the isotherm of the AACH was characteristic of a type IV isotherm with a type H\(_2\) hysteresis loop above 0.4 P/P\(_0\), indicating there existed meso-pores. And BJH from adsorption isotherm (the inset image) displayed that besides a wide pore size at 20.15 nm, the pore sizes of the AACH were mainly centered at 4.78 nm. The results were consistent with the results of SEM of the AACH. It can be seen in Fig. 4 that the AACH was composed by a great number of nanofibers with the width about 500 nm. Moreover from its high-magnification SEM image, it was found that the surfaces of nanofibers were not smooth with a lot of small pores. The results meant that the wide pore sizes at 20.15 nm might be arrived from the accumulations of the nanofibers and the pore sizes at 4.78 nm might be stemmed from the numerous small micropores in the nanofibers. The detailed textural property of the AACH can be seen in the Table 2.

### Table 2

| Samples | BET Surface Area (m\(^2\)/g) | Micropore Area (m\(^2\)/g) | Pore Volume (cm\(^3\)/g) | Average Pore Size (nm) |
|---------|------------------------------|---------------------------|--------------------------|------------------------|
| AACH    | 260.10                       | 53.72                     | 0.48                     | 8.72                   |

### 3.2 Conversion of glucose into HMF

In order to identify the products and calculate the carbon balance on the conversion of glucose, oceans of technologies were adopted, such as GC, HPLC and UV. In all catalytic systems, besides the HMF, tons of other compounds were found, such as glucose, fructose, formic acid, glyceraldehyde and disaccharides. In the case of the base catalyst AACH, Fructose was its main intermediate and its yield was only to 8.5 \(^{\text{c}}\). The yields of other compounds were very low, less than 1.5 \(^{\text{c}}\). For instance, formic acid and levulinic acid, stemmed from the decomposition of HMF, were 1.15 \(^{\text{c}}\) and 0.68 \(^{\text{c}}\). While, In the case of the acid catalysts, such as HCl, the main other compound was formic acid and levulinic acid, which was up to 6.5 \(^{\text{c}}\) and 4.5 \(^{\text{c}}\). The yield of fructose was very low, hard to detect. With the regard to their HMF yields and high glucose conversions (Table 3), it was concluded that many other compounds were not detected. The results were well consisted with many researches\(^{19-21}\). Although many other com-
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Table 3  Conversion of glucose into HMF using some conventional catalysts.

| Entries | Catalysts | Catalyst loading (mg) | HMF Yields (%) | Glucose Conversions (%) | Fructose Yields (%) | Others Yields (%) |
|---------|-----------|------------------------|----------------|-------------------------|--------------------|------------------|
| 1       | No catalyst | 0                      | 1.52           | 12.15                   | 0.52               | 10.11            |
| 2       | AACH      | 300                    | 52.17          | 83.59                   | 8.50               | 22.92            |
| 3       | γ-Fe₂O₃   | 344                    | 2.47           | 60.38                   | 1.23               | 56.68            |
| 4       | γ-Al₂O₃   | 219                    | 5.10           | 76.28                   | 1.42               | 69.76            |
| 5       | HZSM-5    | 300                    | 16.18          | 78.29                   | trace              | 62.11            |
| 6       | H₂SO₄     | 421                    | 22.13          | 86.34                   | trace              | 64.21            |
| 7       | HCl       | 322.5                  | 19.31          | 82.16                   | trace              | 62.85            |
| 8       | CrCl₃•6H₂O | 572                    | 56.36          | 90.15                   | trace              | 33.79            |
| 9       | NH₃•H₂O   | 301                    | 1.38           | 14.51                   | 0.62               | 12.51            |
| 10      | NaOH      | 86                     | trace          | 23.45                   | 1.23               | 21.22            |

* a: 25 wt% sulphuric acid; b: 25 wt% hydrochloric acid; c: 25 wt% ammonium hydroxide

Scheme 1  Possible reaction process of the conversion of glucose.

Hence, in the experiments, all products were classified into four types: HMF, Glucose, Fructose and Others. The results were shown in Table 3. It can be seen that AACH was one of effective catalysts for the conversion of glucose into HMF. Using AACH as the catalyst (Entry 2), the HMF yield was up to 52.17%, the glucose conversion was also to 83.59%. In the absence of any catalyst, there were only 1.52% HMF yield and 12.15% glucose conversion (Entry 1). The results indicated the catalytic activity primarily arise from the AACH, while DMSO and [Bmim]⁺Cl⁻ were acted as the solvent to dissolve glucose and products. Furthermore compared with the heterogeneous acid catalysts γ-Fe₂O₃, γ-Al₂O₃, HZSM-5 (Entry 3-5) and homogeneous acid catalysts H₂SO₄, HCl, CrCl₃•6H₂O (Entry 6-8), AACH not only can keep a moderate HMF yield (52.17%) but also can prevent byproducts from generating (Others yield 22.92%). Using γ-Fe₂O₃, γ-Al₂O₃, HZSM-5, H₂SO₄ or HCl as the catalyst, the HMF yield was only 2.47%, 5.10%, 16.18%, 22.13% or 19.31%, while the Others yield was up to 56.68%, 69.76%, 62.11%, 64.21% or 62.85%. Although the homogeneous acid catalysts CrCl₃•6H₂O had higher HMF yield of 56.36%, the Others yield was also up to 33.79%, which was much higher than that of AACH about 22.92%. Moreover, compared with the basic catalysts NH₃•
H₂O and NaOH, it was also demonstrated that AACH was one of the proper basic catalysts for the conversion of glucose into HMF. In Table 3 (Entry 9), it can be seen that the results under NH₃·H₂O was similar with that without any catalysts, which indicated that weak alkaline catalyst NH₃·H₂O cannot promote glucose converted into HMF. Although using NaOH (Entry 9) could result in the conversion of glucose increase from 12.15% into 23.45%, the HMF could not be found, which suggested strong alkaline catalyst NaOH might not benefit the formation of HMF, which was agreed with the reference 40. As is well known, the process of glucose into HMF mainly obtained two reaction steps, which were isomerization of glucose into fructose and dehydration of fructose into HMF. The isomerization process was the hard and key step. The common strong base, such as NaOH, would significantly inhibit dehydration of fructose into HMF. The common weak base, such as NH₃·H₂O, cannot prompt glucose isomerized into fructose. The result indicated the alkalinity of AACH was preferred to improve glucose converted into HMF, compared with the common base catalysts NaOH and NH₃·H₂O.

### 3.3 Effect of AACH on conversion of fructose into HMF

In order to clearly understand catalytic effect of AACH on the conversion of glucose into HMF, fructose was designed as the raw reaction material and the results were shown in Table 4. According to previous researches, acid catalysts can promote fructose converted into HMF. Our results were consistent with the conclusion. In the absence of any catalysts (Entry 1), the HMF yield and fructose conversion were also up to 83.34% and 91.46% respectively, which were much higher than that of glucose under the AACH or at absence of any catalysts (Table 3). When adding acid catalysts H₂SO₄, HCl, CrCl₃·6H₂O into the reaction system (Entries 3-5), HMF yield and fructose conversion further increase, more than 92.38% and 99%, respectively. However, when basic catalyst AACH was used as the catalyst (Entry 2), HMF yield and fructose conversion was declined significantly from 83.34% and 91.46% of No catalyst to 59.55% and 67.61%, respectively. The results meant that AACH would hinder dehydration of fructose into HMF, which was agreed with the above inference. On other hand, it suggested that basic catalyst AACH possessed high isomerization ability of glucose into fructose.

### 3.4 Effects of catalyst loading, temperature, reaction duration and solvent

The effects of reactional conditions, including catalyst loading, temperature, reaction duration and solvent, were also investigated in the work. Figure 5 shows the effect of catalyst loading on HMF from the conversion of glucose. It can be seen that when the amount of AACH was not more than 0.3 g, both glucose conversion and HMF yield increased with the increase of AACH from 12.15% and 1.52% at absence of AACH to 83.59% and 52.17% at 0.3 g AACH, respectively. When the amount of catalyst AACH was more than 0.3 g, glucose conversion also increased gradually, up to 89.32% at 0.5 g. However, the HMF yield decreased quickly with the increase of AACH from 52.17% at 0.3 g AACH into 39.45% at 0.4g AACH and 28.81% at 0.5 g AACH, indicating that the excessive AACH didn’t benefit glucose converted into HMF. The optimum amount of AACH was 0.3 g in the experiments.

The effect of temperature was shown in Fig. 6. It can be observed that the reaction temperature had significant influence on glucose conversion and HMF yield. When the
undesired byproducts, such as soluble polymer and insoluble reaction were much easier to happen to generate many byproducts. After the reaction temperature was over 120°C, HMF yield decreased into 35.66%. For instance, the temperature was 140°C, the glucose conversion was over 130°C, and the HMF yield decreased into 83.59%. However, the HMF yield at 130°C and 140°C was still increased gradually, from 83.59% (10 h) to 96.38% (10 h). However, HMF yield increased initially, from 8.1% (0.5 h) to 32.73% (2 h), to 50.57% (3.5 h). But when the temperature was up to 4h, HMF yield was to the max, up to 52.17%. Afterwards, time increase resulted in HMF yield decrease enormously, from 48.22% (4 h) to 35.55% (5 h), to 16.88% (10 h), attributed to the formation of more undesired byproducts with the increase of reaction time. Hence, the optimum reaction time was 4 h.

The reaction solvent is also a vital factor on the conversion of glucose into HMF. Hence, a series of common solvents were applied to investigate the effect of solvent. The results were given in Table 5. It can be seen that among these mono-solvent, HMF yield in [Bmim]+Cl− was highest, to 11.45%. The HMF yields in water, dimethyl sulfoxide (DMSO), N, N-dimethylacetylamide (DMAC), N, N-dimethylformamide (DMF) were only 1.59%, 8.73%, 6.37% and 5.23%. The result was ascribed to the unique properties of ionic liquid [Bmim]+Cl−. Firstly, anion Cl− of ionic liquids can accelerate the isomerization of glucose into fructose and decomposition of fructose into HMF due to its alkalinity and nucleophilicity; Secondly, cation [Bmim]+ could stabilize the HMF and avoid side reaction of HMF generate due to its electrophilicity. However, the HMF yield in [Bmim]+Cl− with 11.45% was much lower than that of previous works (more than 40%). The result might be ascribed to high viscosity of ionic liquid [Bmim]+Cl−, which might prevent the raw materials from moving and touching with the catalyst AACH. From the supposition, mixed solvent was used, and the results showed in Table 5 and Fig. 8.

From Table 5, the mixed solvent of [Bmim]+Cl− and DMSO has the best effect on the production of HMF from glucose among these mixed solvents. It can be seen from Fig. 8 that after adding 0.5 g DMSO into 1.5 g [Bmim]+Cl−, the reaction temperature was below 100°C, glucose conversion and HMF yield were both very low, less than 20% and 3.0% respectively. When the reaction temperature was over 100°C, glucose conversion and HMF yield increased significantly, from 18.52% and 2.75% at 100°C into 83.59% and 52.17% at 120°C, respectively. However, when the reaction temperature was over 120°C, the glucose conversion was still increased gradually, from 83.59% at 120°C to 86.67% at 130°C and 93.56% at 140°C. But the HMF yield firstly almost didn’t change (52.17% at 120°C and 51.32% at 130°C), then decreased greatly after the temperature was over 130°C. For instance, the temperature was 140°C, HMF yield decreased into 35.66%. The results indicated that after the reaction temperature was over 120°C, side reactions were much easier to happen to generate many undesired byproducts, such as soluble polymer and insoluble humins. Hence, the optimum reaction temperature was 120°C.

The effect of the reaction times was also investigated. As shown in Fig. 7, it could be observed that glucose conversion increased with the increase of reaction time, from 23.78% (0.5 h) to 75.21% (3 h), to 89.67% (5 h), to 96.38% (10 h). However, HMF yield increased initially, from 8.1% (0.5 h) to 32.73% (2 h), to 50.57% (3.5 h). But when the reaction temperature was over 120°C, glucose conversion and HMF yield were both very low, less than 20% respectively. When the reaction temperature was below 100°C, glucose conversion and HMF yield increased significantly, from 18.52% and 2.75% at 100°C into 83.59% and 52.17% at 120°C, respectively. However, when the reaction temperature was over 120°C, the glucose conversion was still increased gradually, from 83.59% at 120°C to 86.67% at 130°C and 93.56% at 140°C. But the HMF yield firstly almost didn’t change (52.17% at 120°C and 51.32% at 130°C), then decreased greatly after the temperature was over 130°C. For instance, the temperature was 140°C, HMF yield decreased into 35.66%. The results indicated that after the reaction temperature was over 120°C, side reactions were much easier to happen to generate many undesired byproducts, such as soluble polymer and insoluble humins. Hence, the optimum reaction temperature was 120°C.

**Table 5 Effect of various solvents on the conversion of glucose into HMF.**

| Entries | Solvents | HMF Yields (%) |
|---------|----------|----------------|
| 1       | H₂O      | 1.59           |
| 2       | DMSO     | 8.73           |
| 3       | DMA      | 6.37           |
| 4       | DMF      | 5.23           |
| 5       | [Bmim]+Cl− |11.45          |
| 6       | [Bmim]+Cl−/DMSO | 52.17         |
| 7       | DMF/DMSO | 6.15           |

*: The mass ratio of [Bmim]+Cl− and DMSO was 1:1

**: The mass ratio of DMF and DMSO was 1:1
the HMF yield enormously increased from 11.45% into 43.73%. When the mass ratio of DMSO and [Bmim]Cl was to 1:1, the HMF yield was up to the maximum, to 52.17%. Further increasing DMSO mass ratio would arouse the HMF yield decrease. When the mass ratios of DMSO and [Bmim]Cl were to 1.5:1 or 2:0, the HMF yield decreased into 32.24% and 8.73%.

3.5 Recyclability of catalyst
The reusability of catalyst is great important for the practical production of HMF. Hence, the Recyclability of catalyst was also investigated. The method of catalyst recycle was as following: after the reactions, the solid residual was obtained via the centrifugalization. Afterwards, the residual was washing by the ethanol and deionized water at three times respectively. Finally, the catalyst was obtained after the washed solid was dried at 120°C for 12 h and used to the next reaction. Figure 9 shows the results of recycling experiments. It was found that the catalyst AACH had a well stable catalytic activity for the conversion of glucose into HMF. After six reaction runs, there was only a slight decrease in HMF yield and HMF yield was also up to 49.34%.

3.6 Possible catalytic mechanism
According to the results, the reported mechanism and principle of base catalytic reaction, a possible cata-

![Scheme 2](image)

Scheme 2  Possible mechanism of HMF from the conversion of glucose in the reaction system.
lytic mechanism was proposed (shown in Scheme 2). As seen in Scheme 2, a possible base catalytic mechanism was proposed. Firstly, α-glucose was converted into β-glucose. In the step, the base sites of the catalyst AACH and the anions Cl− of ionic liquids [Bnim] + Cl− reacted with α-glucoses and formed the intermediates with five-membered cyclic structures. Afterwards, the intermediates were converted into β-glucoses. Secondly, β-glucose was converted into open glucose. Thirdly, open glucose was converted into fructose. Base sites of the catalyst AACH reacted with open glucoses and formed five-membered cyclic intermediates. After the break of five-membered rings of the intermediates, fructoses were obtained. Finally, Fructose was dehydrated into HMF.

4 Conclusion
In conclusion, the efficient and catalytic production of HMF from glucose has been successfully developed using AACH as the catalyst in the mixtures of [Bnim] + Cl− and DMSO. A moderate HMF yield (52.17%) was obtained at 120°C for 4 h. A series of compared experiments were carried out, such as acid catalysts (γ-Fe2O3, γ-Al2O3, HZSM-5, HCl, H2SO4, CrCl3·6H2O), common basic catalyst (NH3·H2O, NaOH). The results showed that AACH was one of the proper catalysts for the conversion of glucose into HMF, which possessed high isomerization of glucose into fructose and moderate dehydration of fructose into HMF, and can effectively inhibit the side reaction happen, such as polymerization and decomposition of HMF. Furthermore, the recycling experiments were also carried out. It was found that the AACH catalytic system has high catalytic stability. After six reactional runs, the HMF yield about 49.34% was obtained.

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