



Preparation of miscellaneous ammonium aluminum carbonate hydroxide and its effect on the conversion of glucose into 5-hydroxymethylfurfural

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ABSTRACT

An efficient process was developed for the conversion of glucose into 5-hydroxymethylfurfural (HMF). A series of common weak alkalinity solid catalyst, ammonium aluminum carbonate hydroxide (AACH, with formula $\text{NH}_4\text{Al}(\text{OH})_2\text{CO}_3$), was prepared at different condition and used for the conversion of glucose into 5-hydroxymethylfurfural in ionic liquid 1-butyl-3-methylimidazolium chloride ($[\text{Bmim}]\text{Cl}$) and dimethyl sulfoxide (DMSO) mixtures. In those catalyst, the ammonium aluminum carbonate hydroxide prepared at 140 °C for 36 h was found to be the best catalyst for this transformation and the optimal HMF yield was 42.35% at 120°C for 4h. The recycling experiments showed that the AACH owned a well stable catalytic activity for the conversion of glucose into HMF. After six reaction runs, its catalytic activity didn't loss significantly and a moderate HMF yield of 39 % was also obtained. In addition, various reaction conditions about the preparation for AACH, including material ratio, temperature, reaction time, were also investigated.

Keyword: AACH, glucose, 5-hydroxymethylfurfural (HMF), catalytic activity

INTRODUCTION

With the depleting of fossil resources and growing concerns about environmental pollution, global warming, biomass with an estimated global production of around 1.0×10^{11} tons per year provides a ideal and promising alternative source to produce fuels and chemicals[1-3]. Carbohydrates are the major components of biomass. Hence, catalytic conversion of carbohydrate into high-value chemical and fuels is significantly both in science and commerce[4].

5-hydroxymethylfurfural (HMF) is an important biomass-derived chemicals, which can be synthesized from carbohydrates, such as glucose, fructose and xylose. Simultaneously, HMF is an important platform intermediate, because it can be converted into many useful high-value chemicals and liquid fuels such as levulinic acid (LA), 2,5-bishydroxymethylfurfural, 2,5-diformylfuran (DFF), 2,5-dihydroxymethylfuran (DHMF), 2,5-dimethyl tetrahydrofuran (DMTHF), 2,5-furandicarboxylic acid (FDCA), 2,5-dimethylfuran (DMF), 5-ethoxymethylfurfural (EMF), ethyl levulinate (EL) and linear alkanes[5-7]. Thus, much more attention are paid to the conversion of sugars into HMF.

Recently, glucose and fructose are the two main studied objects for the production of HMF. Many works[8-10] demonstrated fructose can be easily converted into HMF under proper catalyst. However the fructose is very expensive and rare. So the fructose is not the optimal choice. Glucose is another saccharides, which is very cheap and available[11]. But many catalytic system of the conversion into HMF is hard or ineffective to convert glucose into HMF[12]. Hence, it is still challenging to develop new catalytic system for the efficient catalytic conversion of glucose into HMF.

Since Zhao *et al.*[13] found that CrCl_2 has well catalytic activity for the conversion of glucose into HMF in ionic liquid 1-ethyl-3-methylimidazolium with a high HMF yield of 69%, people have been mainly aimed at various acid catalyst, such as metal chlorides, solid acid catalyst, H-zeolites, acidic cation-exchange resins, heteropoly acids and carbonaceous catalysts. Other typical catalysts was few studied. Presently, Deng *et al.*[14] found that the alkalinity of catalysts can promote the isomerization of glucose into fructose. Many researches have demonstrated that the catalytic process of HMF obtained from glucose decomposition should be divided into two steps : isomerization of glucose into fructose and dehydration of fructose into HMF[15-17]. The process was showed in Fig. 1. However, the aim of the report worked by Deng *et al.* was to convert glucose into polyols. Whether glucose can be converted into HMF under alkaline catalyst wasn't studied. Hence, it is urgently necessary to search for an easy-prepared and low-cost solid alkaline catalyst for the conversion of glucose into HMF.

AACH is common weak base solid compound, which is easy to prepare and usually used as the precursor for industrial catalyst Al_2O_3 [18]. So, it is easy to get and the price is very low. In the work, AACH of different properties were prepared at different condition (different temperature, different time, different material ratio) and these AACH were used as the reaction catalyst to produce HMF from glucose conversion in ionic liquid [Bmim]Cl and DMSO mixtures. Its catalytic performance in the conversion of glucose into HMF was compared with a series of catalyst, such as $\text{Cu}_2(\text{OH})_2\text{CO}_3$, $4\text{MgCO}_3\cdot\text{Mg}(\text{OH})_2\cdot 5\text{H}_2\text{O}$, $3\text{Zn}(\text{OH})_2\cdot 2\text{ZnCO}_3$, Mg/Al-LDHS, Zn/Al-LDHS and so on.

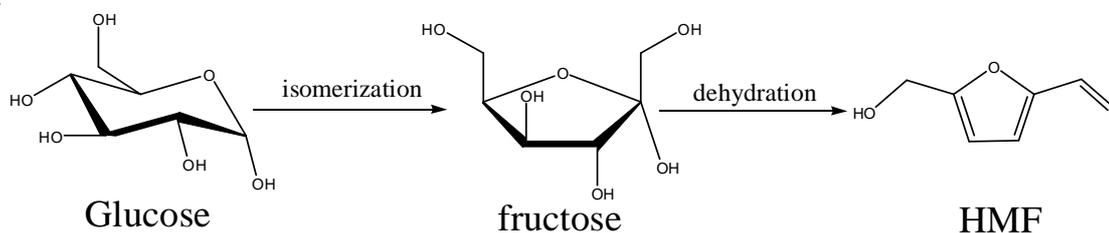


Fig. 1. The process of the conversion of glucose into HMF

EXPERIMENTAL SECTION

Materials and Chemicals

Ionic liquids, 1-butyl-3-methylimidazolium chloride ([Bmim]Cl, AR) was purchased from Shanghai Cheng Jie Chemical Co. Ltd. (Shanghai China). HMF (99%), $3\text{Zn}(\text{OH})_2\cdot 2\text{ZnCO}_3$, $\text{CH}_2\text{O}_7\text{Zr}_2$ were 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.

Catalysts preparation

AACH was prepared via hydrothermal synthetic method according to the previous procedures with some modifications[19]. In a typical synthesis, 0.01 mol $\text{Al}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ and 0.08~0.28 mol urea were added into 50 mL distilled water under vigorous stirring to form a homogeneous solution. Then, the solution was transferred into a 100 mL Teflon-lined stainless autoclave, sealed and then heated at 120~160°C for 12~60h. Afterwards, the autoclave was cooled to room temperature naturally. The product was collected through centrifugation and washed several times with deionized water. Finally, the AACH samples were obtained by drying the product in a vacuum at 100 °C for 12 h.

Catalysts characterization

The structure and phase purity of samples were determined by Panalytical X-ray diffraction (XRD, X'Pert PRO MPD) analysis with Cu-K α radiation ($\lambda=1.5406 \text{ \AA}$). The data were recorded over 2θ range of 10-80°. The FT-IR spectra were recorded by a Nicolet 460 spectrometer using the KBr powder technique with diffuse reflectance sampling accessory at a resolution of 4 cm^{-1} at room temperature.

Typical procedure of HMF from glucose

The catalytic processes were carried out in the tube of 18mm \times 180mm with a lid. In the typical run, 0.1g glucose and 0.3g AACH were added into the mixture of 1g ionic liquid [Bmim]Cl and 1g DMSO. Subsequently, the tube was transferred into a 120°C oil bath and was stirring at the speed of 500 rpm for 4h. At the end of the reaction, 10 ml deionized water was added into the reaction mixture to cool and dilute the reaction mixture. Finally, the solution was centrifuged at 10000 rpm for 5 min. The clear liquid was sent to further analyze.

Analysis

The amount of HMF was detected by ultraviolet full-wave scanning spectrophotometer (TU-1810, Beijing Purkinje

General Instrument CO. Ltd., Beijing China) at the ultraviolet wavelength of 284nm via external standard method. The content of glucose was checked by HPLC (Agilent 1200) equipped with a refractive index detector with a ion exclusion column (300 mm × 7.8 mm, Aminex HPX-87H) at 60°C. The condition of mobile phase was 0.007 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:

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

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

RESULTS AND DISCUSSION

Catalyst characterization

The FT-IR spectra of different type of AACH products are shown in Fig. 2. In the Fig. 2, there are four typical peaks of O-H, N-H, C-O, Al-O. The AACH exhibits a wide signal nearby 3443 and 985 cm⁻¹ due to the ν OH and δ OH vibrations, respectively. The peak at 3175, 3018 and 2840 cm⁻¹ are ascribed to ν NH stretching vibrations, and the bands at 1828 and 1723 cm⁻¹ are due to δ NH stretching vibrations. The ν₃ of CO₃²⁻ vibrations bands was observed at 1545, 1452 and 1382 cm⁻¹, and the ν₁, ν₂ and ν₄ of CO₃²⁻ vibrations bands was observed at 1105, 850 and 760 cm⁻¹. Finally, the three bands at 751, 630, and 484 cm⁻¹ represent the vibration mode of AlO₆. All the absorption bands in Fig. 2 are consistent with the reported values for AACH [19].

From the previous work, the NH₄⁺ of AACH can promote the conversion of glucose into HMF. As was shown in Fig. 2, all the AACH of different temperature had wide signal at 3175, 3108, 2840, 1723cm⁻¹ due to the vibrations of N-H. However, the AACH, which was prepared at 140°C, had a strongest band at 3175, 3108, 2840, 1723cm⁻¹. Especially, the band at 1723cm⁻¹ was very clear. The FT-IR spectra of different type of AACH had demonstrated that the AACH which was prepared at 140°C had a high catalytic activity on the conversion of glucose into HMF.

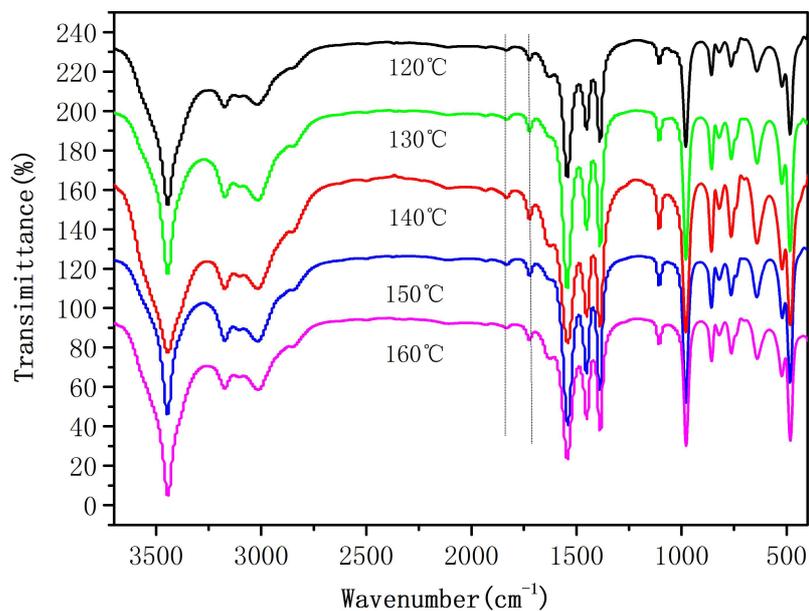


Fig. 2 The FT-IR of all the AACH of different temperature

The Mg/Al-LDHS and Zn/Al-LDHS were also characterized by the FT-IR. From the Fig. 3, the FT-IR spectra of Mg/Al-LDHS and Zn/Al-LDHS shows many peaks due to their special structure. The bands at 3460, 1630 cm⁻¹ were assigned to O-H stretching of water molecules in the layers and the O-H bending mode. The band at 1350 cm⁻¹ belong to the stretching modes of CO₃²⁻. However, compared with the FT-IR spectra of AACH, there are no peaks at 3175, 3108, 2840, 1723cm⁻¹, belonging to the vibrations of N-H. Especially, no peak was found at 1723 cm⁻¹ from the FT-IR of Mg/Al-LDHS and Zn/Al-LDHS.

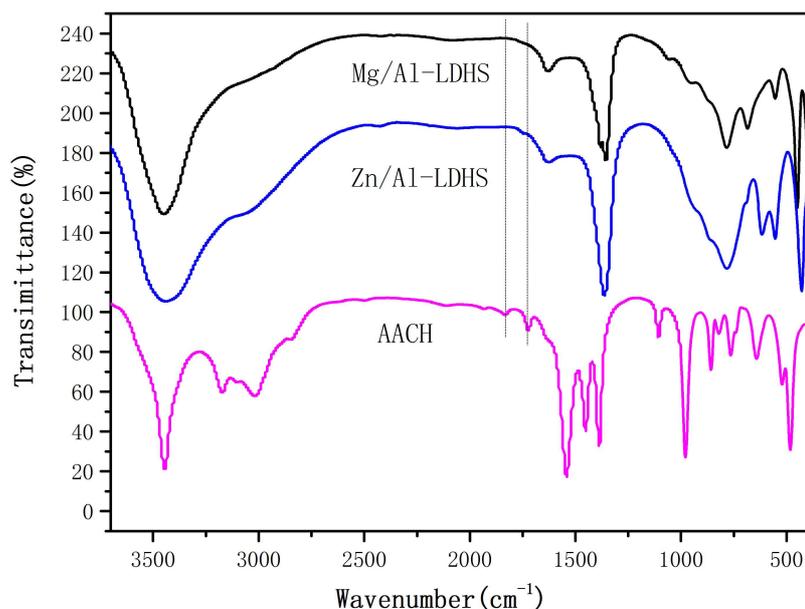


Fig. 3 The FT-IR of the same type of catalysts

The XRD patterns of different type of AACH products are shown in Fig. 4. All the XRD pattern of these AACH show strong diffraction peaks at 2θ angles of 10-70° and All the diffraction peaks are indexed into the orthorhombic AACH and the high-crystalline AACH is in good agreement with JCPDS Card 042-0250. This phenomenon can demonstrate that all the AACH can be synthesized among these temperature. As can be seen from Fig. 4, when the temperature was between 120°C and 140°C, the intensity of diffraction peaks increased with the increase of the temperature of catalyst preparation. Certainly, when the temperature was 140°C, the intensity of diffraction peaks was the strongest. But after the temperature of catalyst preparation was higher than 140°C, the intensity of diffraction peaks decreased with the increase of the temperature of catalyst preparation.

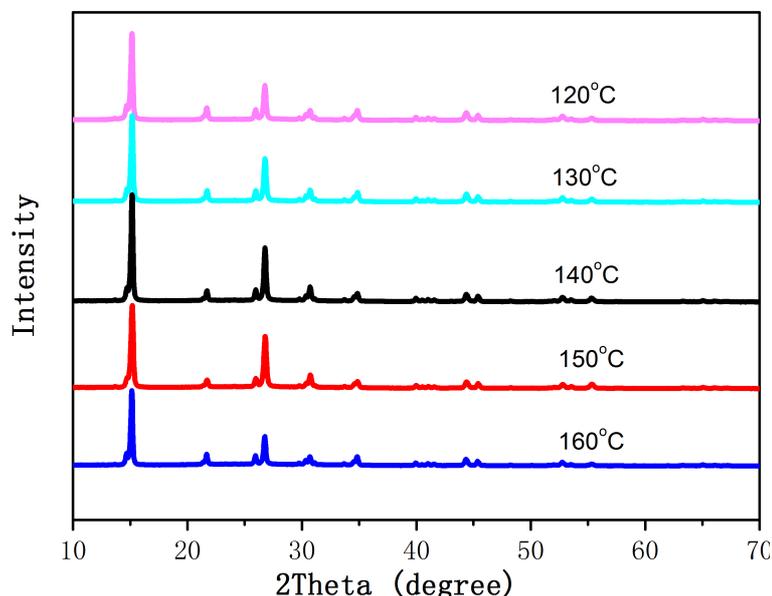


Fig. 4 The XRD patterns of different type of AACH products

Conversion of glucose into HMF by different alkali salt

We explored the effects of numerous acid catalysts and alkali catalysts on the conversion of glucose into 5-HMF in a mixed solvent of [BMIM]Cl and DMSO at 120°C for 4h, all the results were shown in Table 1. These catalysts includes $\text{Cu}_2(\text{OH})_2\text{CO}_3$, $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$, $3\text{Zn}(\text{OH})_2 \cdot 2\text{ZnCO}_3$, $\text{CH}_2\text{O}_7\text{Zr}_2$, Mg/Al-LDHS, Zn/Al-LDHS, $\text{Al}_2\text{O}_3\text{-NH}_3$, Al_2O_3 and AACH. From the Table 1, it can be seen that AACH was one effective catalysts for the conversion of glucose into HMF in a mixed solvent of [BMIM]Cl and DMSO. The yield of HMF was 42.35% and the glucose conversion was also up to 80.08% by using AACH as catalyst at 120°C for 4h. Certainly, a blank test

was done without catalyst. About 1.49% HMF yield and 13.04% glucose conversion were attained after 4h at 120°C. From these information, it can be seen that glucose was hard to be converted into HMF without catalyst. When the catalyst was $\text{Cu}_2(\text{OH})_2\text{CO}_3$, the yield of HMF and the conversion of glucose were 10.29% and 30.72%, respectively. The other catalysts such as $4\text{MgCO}_3\cdot\text{Mg}(\text{OH})_2\cdot 5\text{H}_2\text{O}$, $3\text{Zn}(\text{OH})_2\cdot 2\text{ZnCO}_3$ and $\text{CH}_2\text{O}_7\text{Zr}_2$, all have a low catalytic activity on the dehydration of glucose into HMF with less than 6% HMF yield and 20% glucose conversion. Surprisingly, when the catalysts were these catalysts, such as $4\text{MgCO}_3\cdot\text{Mg}(\text{OH})_2$ and $\text{CH}_2\text{O}_7\text{Zr}_2$, the HMF yield and glucose conversion were all less than the yield and glucose without catalyst. It may be result from two reasons. On the one hand, these catalyst have less catalytic activity on the dehydration of glucose into HMF. On the other hand, these catalyst were alkali catalysts and when they react with glucose in a mixed solvent of [BMIM]Cl and DMSO, the alkalinity of AACH cause acidity of the reaction system decrease a little. As is know for us, acidity is benefited to convert fructose into HMF. Certainly, we also did some experiments and the proposal is confirmed by the pH value of reacted solution, which is up to 8.3.

To the best of our knowledge, the AACH and the hydrotalcite could be mutual transformation in some condition when the hydrotalcite was prepared. According to these, a assumption that these hydrotalcite may have a good catalytic activity on the dehydration of glucose into HMF was attained. So the other type catalyst, such as Mg/Al-LDHS and Zn/Al-LDHS, were prepared to catalyze the glucose to HMF. But from the Table 1, we found that Mg/Al-LDHS and Zn/Al-LDHS also have low catalytic activity with less than 3% HMF yield. The results also indicated that the construction of AACH may be not the main reason for the glucose into HMF with a high HMF yield. It is very consistent with previous work.

From the previous work, the NH_4^+ was the key effect when AACH catalyze the glucose into HMF. In order to further demonstrate the conclusion, the catalysts Al_2O_3 and $\text{Al}_2\text{O}_3\text{-NH}_3$ were applied into the glucose into HMF. When the catalyst was acid catalyst Al_2O_3 , the yield of HMF was 4.98% and the conversion of glucose was 77.03%. But when using $\text{Al}_2\text{O}_3\text{-NH}_3$ as catalyst, the yield of HMF was 10.53% and the conversion of glucose was 80.05%. This also demonstrate the effect of NH_4^+ .

Table1. Conversion of glucose into HMF by different alkali catalysts

Entry	catalyst	HMF yield (%)	Glucose Conversion (%)
1	No catalyst	1.49	13.04
1	$\text{Cu}_2(\text{OH})_2\text{CO}_3$	10.29	30.72
2	$4\text{MgCO}_3\cdot\text{Mg}(\text{OH})_2\cdot 5\text{H}_2\text{O}$	0.84	10.63
3	$3\text{Zn}(\text{OH})_2\cdot 2\text{ZnCO}_3$	5.59	19.56
4	$\text{CH}_2\text{O}_7\text{Zr}_2$	1.19	8.58
5	Mg/Al-LDHS	2.05	10.35
6	Zn/Al-LDHS	2.42	11.96
7	$\text{Al}_2\text{O}_3\text{-NH}_3$	10.53	80.05
8	Al_2O_3	4.98	77.03
9	AACH	42.35	80.08

Reaction condition: glucose (0.1g); catalyst (0.3g); [Bmim]Cl (1g); DMSO (1g); 120 °C; 4 h.

Effect of the temperature for catalyst preparation

As can be seen from Fig. 5, the temperature for catalyst preparation has a significant influence on the yield of HMF, but has a low influence in conversion. The experiment about the preparation for AACH were conducted at 120°C, 130°C, 140°C, 150°C, 160°C to study the effect of the temperature for catalyst preparation on the yield of HMF in a mixed solvent of [BMIM]Cl and DMSO at 120°C for 4h. when the temperature of preparation was 120°C, only 27.3% HMF yield and 73.15% glucose conversion were gained after 4h, respectively. At the beginning of temperature rise, the glucose conversion and HMF yield increased to 79.43% and 28.94% slowly at 130°C. When the temperature for catalyst preparation was 140°C, HMF yield was up to maximum with 42.17% HMF yield. But when the temperature exceeded 140°C, the yield of HMF decreased sharply with the increase of temperature, from 42.17% at 140°C to 31.50% at 150°C and 25.91% at 160°C. Surprisingly, when the temperature for catalyst preparation changed from 120°C to 160°C, the conversion of glucose did not change largely. The maximal glucose conversion was 80.08% at 140°C and the minimal glucose conversion was 73.15% at 120°C. The different temperature for catalyst preparation may result in changing of the amount of NH_4^+ , the detailed mechanism is still under research. Therefore, 140°C was chosen as the optimal reaction temperature for catalyst preparation.

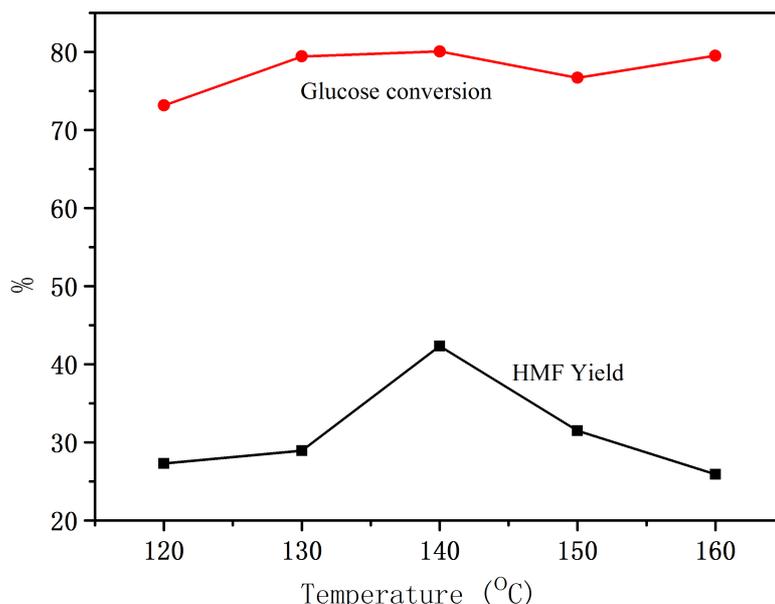


Fig. 5. Effect of the temperature of catalyst preparation on the conversion of glucose into HMF

Effect of the material ratio of catalyst preparation

In order to understand clearly the reaction process of catalyst preparation, the material ratio of catalyst preparation (mole ratio of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{CO}(\text{NH}_2)_2$) was also investigated in the work. All the results were shown in Fig. 6. From the Fig. 6, it can be seen that the material ratio of catalyst preparation also play significant influence on the yield of HMF, when the reaction was conducted in a mixed solvent of [BMIM]Cl and DMSO at 120 °C for 4h. Six catalysts from six mole ratio, such as 1:8, 1:12, 1:16, 1:20, 1:24, 1:28, were conducted to study the effect of the material ratio on the conversion of glucose into HMF in a mixed solvent of [BMIM]Cl and DMSO. When the mole ratio of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{CO}(\text{NH}_2)_2$ was 1:8, the yield of HMF was 33.32%. With the increasing of the amount urea (the decrease of the mole ratio of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{CO}(\text{NH}_2)_2$), the yield of HMF increased slowly. When the mole ratio was 1:20, the yield of HMF was up to maximum with 42.17% HMF yield. Further increasing the urea, we could find that the HMF yield do not decreased sharply and when the mole ratio was 1:24, the HMF yield was 39.04%. From the Fig. 2, it also can be seen that the HMF yield almost do not change and was kept in 38%. Possibly, when the mole ratio was 1:20, the amount of urea has reached the saturation, so that the construction and NH_4^+ do not change. Therefore, due to economic concerns, the appropriate material ratio was 1:20.

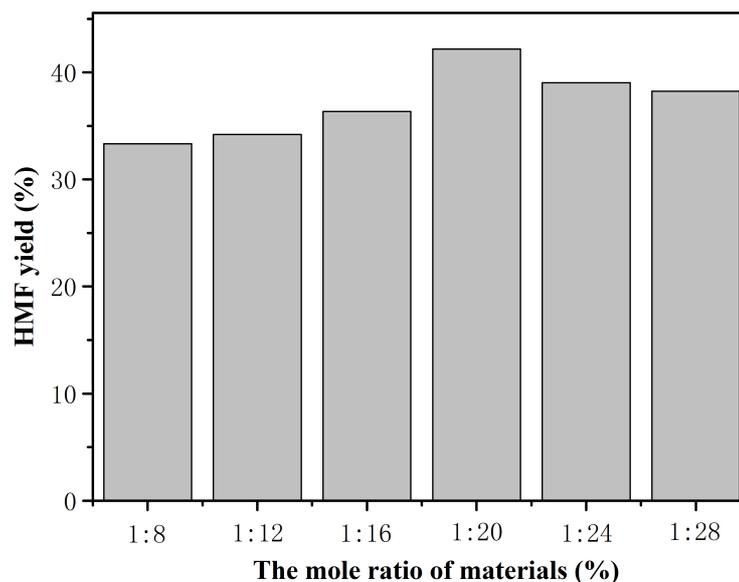


Fig. 6. Effect of the material ratio of catalyst preparation on the conversion of glucose into HMF

Effect of the reaction time of catalyst preparation

Once the reaction temperature for catalyst preparation and the material ratio of catalyst preparation were chosen, the reaction time were investigated at 12h, 24h, 36h, 48h, 60h and all the HMF yields with different time were recorded.

As present in Fig. 7, when the time of catalyst preparation was 12h, 79.24% glucose conversion and 22.75% HMF yield were attained at 120°C for 4h. in a mixed solvent of [BMIM]Cl and DMSO. Obviously, from 12h to 36h, the HMF yield increased quickly, but the glucose conversion almost did not increase. When the time was extended to 36h, the HMF yield was up to 42.17% and the glucose conversion was 80.08%. Further increasing reaction time of catalyst preparation from 36h to 60h, the glucose conversion changed to 82.47%, but the HMF yield decreased to 40.12%. From the above analysis, the optimal reaction time of catalyst preparation was 36h.

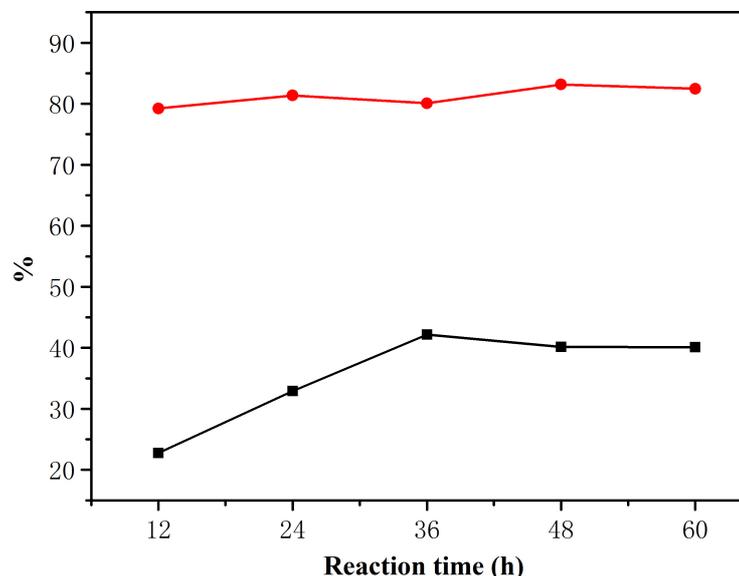


Fig. 7. Effect of the reaction time of catalyst preparation on the conversion of glucose into HMF

Recyclability of catalyst

Catalyst recycling is important to evaluate the catalyst performance and is essential for large-scale industrial production. From previous research, used AACH has poor performance of HMF production obtained from glucose, so the recycle AACH should be used as the recycling reaction catalyst. The detailed recycling experiments are as follow: AACH was separated for the reactional mixture, washed with deionized water at more than 6 times, dried at 100°C for 6h in a vacuum. And the product (used AACH) was impregnated with 25 wt% ammonia water to prepare the recycle AACH. Subsequently, the recycle AACH was added into fresh [Bmim]Cl and DMSO at the same reaction condition and reused via the above process. The results are shown in Fig. 8. It shows that the recycle AACH has well catalytic performance of glucose conversion into HMF. After six reaction run, the HMF yield was still close to 39%, up to 39.62%.

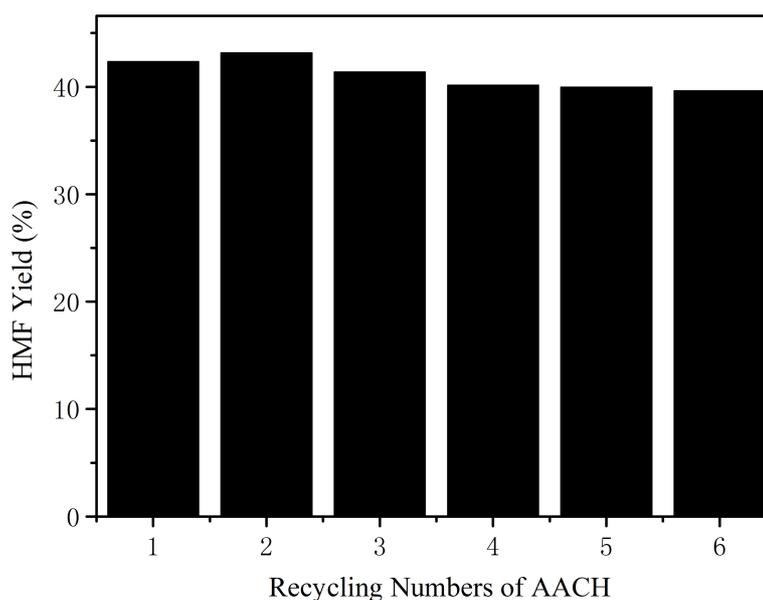


Fig. 8 Results of the recyclability of Recycle AACH

CONCLUSION

In summary, a series of AACH was prepared at different condition, such as different temperature, different mole ratio, different time. Subsequently, these catalyst AACH with different properties were used for the conversion of glucose into 5-hydroxymethylfurfural in ionic liquid 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) and dimethyl sulfoxide (DMSO) mixtures at 120°C for 4h. The optimal catalyst was prepared at 140°C for 36h and the mole ratio of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{CO}(\text{NH}_2)_2$ was 1:16. Certainly, the optimal HMF yield was 42.35% when the optimal AACH was used to catalyze the glucose into HMF. The catalyst which has been processed could be recycled with stable catalytic activity and there was about 39% HMF yield after six reaction runs.

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