Direct Conversion of Glucose to 5-Hydroxymethylfurfural (HMF) Using an Efficient and Inexpensive Boehmite Catalyst in Dimethyl Sulfoxide

Zhe Tang and Jianhui Su *

With the aim of developing an efficient and inexpensive catalyst for the production of HMF from glucose, a solid Lewis acid catalyst γ-AlOOH, a common industrial catalyst with easy preparation and low price, was used as the sole catalyst to directly synthesize 5-hydroxymethylfurfural (HMF) from glucose in dimethyl sulfoxide. Various reaction parameters, such as catalyst loading, temperature, reaction duration, and solvent, were investigated. An impressive HMF yield of 61.2% was obtained at the reaction conditions of 130 °C for 3 h. Furthermore, HMF yields from other carbohydrates such as fructose (44.8%), cellulose (50.3%), maltose (53.6%) and sucrose (62.2%) could be achieved using γ-AlOOH as a catalyst. More importantly, the catalyst γ-AlOOH could be reused several times without the loss of its catalytic activities. After five reaction runs, an HMF yield of 57.2% was obtained.

Keywords: Heterogeneous catalysis; Carbohydrates; HMF; Boehmite

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INTRODUCTION

The diminishing of petroleum resources and the growth of energy demand combined with growing concerns about global warming and environmental pollution has made the efficient utilization of renewable lignocellulosic biomass significant in both academic studies and industrial applications (Caes *et al.* 2015; Li *et al.* 2019). Within the utilization of lignocellulosic biomass, the conversion of glucose into value-added chemicals is significantly important (Eblagon *et al.* 2016; Shamsul *et al.* 2018), since glucose is the most abundant component in lignocellulosic biomass and the most available and low-cost six carbon monosaccharide (DaVià *et al.* 2017). Among various value-added chemicals, HMF (5-hydroxymethyl-furfural) is considered as one of the top 10 platform chemicals, which can be used as a raw material to produce fine chemicals and other materials to replace or minimize fossil-based products, such as 2,5-diformylfuran acid, 2,5-furandicarboxylic acid, and 2,5-dimethyl-furan (Martínez-Vargas *et al.* 2017; Siankevich *et al.* 2015; Zhang and Deng 2015). A review of the potential application of HMF has been summarized by Rosatella *et al.* 2011.

Both homogeneous and heterogeneous catalysis have been considered to produce HMF from glucose. The used homogeneous catalysts mainly contained metal salts, ionic liquid, mineral acid, inorganic acid, and organic acid (Tong *et al.* 2011; Zakrzewska *et al.* 2011; Yang *et al.* 2012; Jain *et al.* 2015). Compared with homogeneous catalysis, heterogeneous catalysis has been increasingly regarded as the most promising to convert glucose into HMF in terms of the separation and recycling of catalysts (Dhepe and Fukuoka 2008; Zhang *et al.* 2016). Numerous environmentally benign heterogeneous solid acid actalysts, such as zeolite-based catalysts, aluminium oxide-based catalysts, SO_4^{2-}-based catalysts, doped catalysts, niobium-based catalysts, carbon-based catalysts, polymer-based catalysts, and phospate-based catalysts, have been developed to synthesize HMF from glucose under various reaction media including ionic liquids, organic solvents, biphasic system, and water-contained systems (Dijkmans *et al.* 2013; Hu *et al.* 2013a; Liu *et al.* 2015; Chen *et al.* 2016; Sun *et al.* 2016; Catrinck *et al.* 2017; Li *et al.* 2017; Lopes *et al.* 2017). Although HMF yields of *ca.* 25% to 70% were obtained in the catalytic systems, they tend to need high reaction temperatures of approximately 160 °C to 200 °C, or the preparations of the catalysts are complicated (Crisci *et al.* 2010; Maldonada *et al.* 2017), which would allow for the side reaction to easily occur and they are hard to apply in the industry of HMF manufacture. Hence, it is necessary to seek a catalytic system that uses an efficient and inexpensive catalyst under a mild reaction temperature to catalyze glucose.

It is generally argued that the conversion of glucose into HMF is a tandem reaction: isomerization of glucose into furanoside fructose and dehydration of furanoside structure of fructose into HMF. It is also generally believed that the isomerization of glucose into fructose is the crucial and rate-determining step in the process of glucose conversion (Delidovich and Palkovits 2016; Li *et al.* 2016; Graça *et al.* 2017). Isomerization of glucose into fructose can be more easily promoted by Lewis acid, bases, and enzymes due to the strong interactions between these types of catalytic activity centers (Lewis acid sites or base sites or enzymatic activity sites) and hydroxyl/carbonyl moieties that are present in aldoses (Saravanamurugan *et al.* 2013; Rajabbeigi *et al.* 2014; Delidovich and Palkovits 2015). Brønsted acid is more effective in improving fructose dehydration into HMF (Hou *et al.* 2018; Xia *et al.* 2018). Moreover, it has also been demonstrated that Lewis acid has moderate catalytic activity on the dehydration of fructose into HMF (Wei and Wu 2017; Jiang *et al.* 2018). In addition, some solvents also have some capacity to improve the dehydration of fructose into HMF, such as ionic liquids and aprotic organic solvents due to their interactions with HMF *via* solation and high solubility for sugars (Li *et al.* 2012a; Gomesa *et al.* 2017). Compared with the high price of ionic liquids, the aprotic organic solvent dimethyl sulfoxide is a low-cost and commonly used solvent. Therefore, these results inspired us that using DMSO and Lewis acid catalysts as the reaction system can be effective to promote the conversion of glucose into HMF.

It is known that Boehmite (γ-AlOOH) is one of the Al_2O_3 precursors and one of the typical Lewis acid catalysts. More importantly, it is easily prepared and has high hydrothermal stability (Wang *et al.* 1998; Sanchez-Valente *et al.* 2003; Chiche *et al.* 2008; Tang *et al.* 2012, 2013). Hydrothermal stability of the catalyst is quite important because water will be produced throughout the process of the dehydration of fructose into HMF, which means that the catalysts used on the conversion of glucose into HMF must possess excellent hydrothermal stability to maintain catalytic stability. Just from the angle of γ-AlOOH with high hydrothermal stability, Takagaki *et al.* (2014) used γ-AlOOH as the catalyst on the transformation of sugars (C_3 sugars to C_6 sugars) in water system and obtained excellent reaction results. Forty-percent lactic acid and HMF was obtained when glucose was used as the raw material. It was also demonstrated that Boehmite was suitable to catalyze a variety of reactions including isomerization, dehydration, and hydration in water. The results suggested that γ-AlOOH could be an efficient catalyst to convert glucose or other carbohydrates into HMF. As far as the authors know, there have been no reports on conversion of glucose or other carbohydrates into HMF catalyzed by γ-AlOOH. On the other hand, unlike other best-behavior heterogeneous catalysts such as doped catalysts, carbon-based catalysts, and polymer-based catalysts, γ-AlOOH is a common industrial catalyst with easy preparation and low price. Thus, it is a more promising catalyst for industry scale production of HMF from carbohydrates.

In this work, γ-AlOOH was prepared and used as the sole catalyst to produce HMF from glucose assisted by DMSO as a reaction solvent under mild reaction conditions. Various reaction parameters, including reaction durations, reaction temperature, catalytic loading, and reaction solvents were investigated. In addition, the conversions of other polysaccharides, such as maltose, sucrose, and cellulose, into HMF were considered.

EXPERIMENTAL

Materials

The HMF (99%) was obtained from Shanghai Aladdin Reagent Co., Ltd. (Shanghai, China). Other reagents used were of analytical grade and obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai Shi, China) and used as received.

Catalysts preparation

In synthesis, 15 mmol aluminum nitrate nonahydrate were added into 50 mL of deionized water. Then, 30 mmol ammonium hydrogen carbonate was slowly added under a magnetic stirring with 800 rpm. After formation of a clear solution, 25% ammonia water was slowly added until the pH reached 9. Afterwards, the mixture reaction system was transferred into a 100-mL Teflon-lined stainless autoclave, sealed, and then heated at 150 °C for 12 h. Subsequently, the autoclave was naturally cooled to room temperature. The product was collected through centrifugation and washed several times with deionized water. Finally, the sample was obtained through vacuum-drying the product at 80 °C for 24 h.

Methods

Catalysts characterization

The phase structure of the sample was analyzed using Panalytical X-ray Powder Diffraction (XRD) with Cu-Kα radiation (λ = 1.5406 Å). The data were recorded within a 2θ range of 5^{o} to 80^{o}. The sample was further evaluated by Fourier transform infrared (FTIR) spectra (Nexus FTIR; Nicolet, Madison, WI, USA) to confirm its composition over the wave number range of 4000 cm^{-1} to 500 cm^{-1} with a scan rate of 0.6329 cm/s

The textural property of the sample was investigated *via* nitrogen adsorption-desorption experiments measured using a Micromeritics ASAP 2020 system (Micromeritics Instrument Corp., Norcross, GA, USA). The specific surface areas and pore size distributions of the samples were calculated using the Brunauer-Emmett-Teller (BET) equation and Barrett-Joyner-Halenda (BJH) method, respectively. The morphology and microstructure of the samples were further observed through transmission electron microscopy (TEM; JEM-2100UHR; JEOL Ltd., Tokyo, Japan). The thermal gravimetric analyses (TGA) of the samples were performed at a heating rate of 10 °C/min under air-atmosphere (SDT Q600; TA Instruments, Newcastle, DE, USA).

Lewis and Brønsted acidic sites were investigated *via* FTIR pyridine adsorption technique (Py-FTIR; Nicolet, Madison, WI, USA) (Li *et al.* 2012b). The IR spectra were recorded at a resolution of 4 cm^{-1} in the range of 1700 cm^{-1} to 1400 cm^{-1}. Prior to measurement, the samples were degassed in air at 150 °C for 5 h, cooled down, and then adsorbed in the saturated pyridine atmosphere at room temperature for 5 h. After adsorption, the infrared spectrum was recorded with the sample temperature fixed at 100 °C while outgassing. The amount of Lewis acid sites was determined on the basis of the integral absorbance of the characteristic band at 1450 cm^{-1} by using integrated molar extinction coefficient 2.22 cm mmol^{-1} (Emeis 1993; Saravanan *et al.* 2015).

Typical procedure of HMF from glucose

The experiments were conducted in an 18 mm × 180 mm glass tube with a lid under the oil bath. In the process, 100 mg glucose and 100 mg catalyst were added into 2.5 g DMSO under a magnetic stirring. After forming a homogeneous solution, the mixtures were heated at 130 °C for 3 h under a magnetic stirring at 800 rpm. Afterwards, the reaction mixtures were quickly cooled to room temperature *via* an addition of 20 mL cold deionized water. Then, the forming mixtures were centrifuged at 10,000 rpm for 5 min and weighed. The clear liquid was collected. It was diluted 150 to 200 times by the deionized water and then the solution was ready to be analyzed.

Analysis

The HMF was analyzed using high performance liquid chromatography (HPLC; Agilent 1200; Agilent Technologies, Palo Alto, CA, USA) equipped with an ultraviolet detector (UV-9600; Beijing Purkinje General Instrument Co., Ltd., Beijing, China) at the ultraviolet wavelength of 284 nm. The amount of HMF was checked *via* the external standard method. Glucose, fructose, disaccharides, levulinic acid and formic acid were also checked *via* HPLC outfitted with a refractive index with an ion-exclusion column (300 mm × 7.8 mm, Aminex HPX-87H; Bio-Rad, Beijing, China) at 60 °C. The other compounds such as glyceraldehyde were detected using gas chromatography (GC; GC1690; Jiedao, Zhejiang, China), and their contents were also measured via the external standard methods. The HMF yield and conversion of glucose were calculated according to the following equations:

$$\text{Glucose conversion}(\%) = 100\% - \frac{mole\ of\ glucose}{mole\ of\ starting\ glucose} \times 100\% \tag{1}$$

$$\text{HMF yield}\ (\%) = \frac{mole\ of\ HMF}{mole\ of starting\ \ glucose} \times 100\% \tag{2}$$

RESULTS AND DISCUSSION

Characterization of the Catalyst

The phase structure of the sample was checked *via* powder XRD (Fig. 1). Its diffraction peaks were assigned to an orthorhombic γ-AlOOH with the mean crystallite size of 14.5 nm (JCPDS Card 021-1307). No peaks from other phases were observed, which indicated the high purity of the catalyst. Further evidence on the formation of γ-AlOOH was derived from the result on its FTIR analysis. Figure 2 shows that the bands at 3310 cm^{-1}, 3090 cm^{-1}, 1072 cm^{-1}, and 1162 cm^{-1} were assigned to the ν_{as} (Al)O-H, ν_s (Al)O-H, δ_s Al-O-H, and δ_{as} Al-O-H vibrations, respectively. The bands at 751 cm^{-1}, 630 cm^{-1}, and 484 cm^{-1} belonged to the vibration mode of AlO_6. All the results revealed that γ-AlOOH had been successfully prepared.

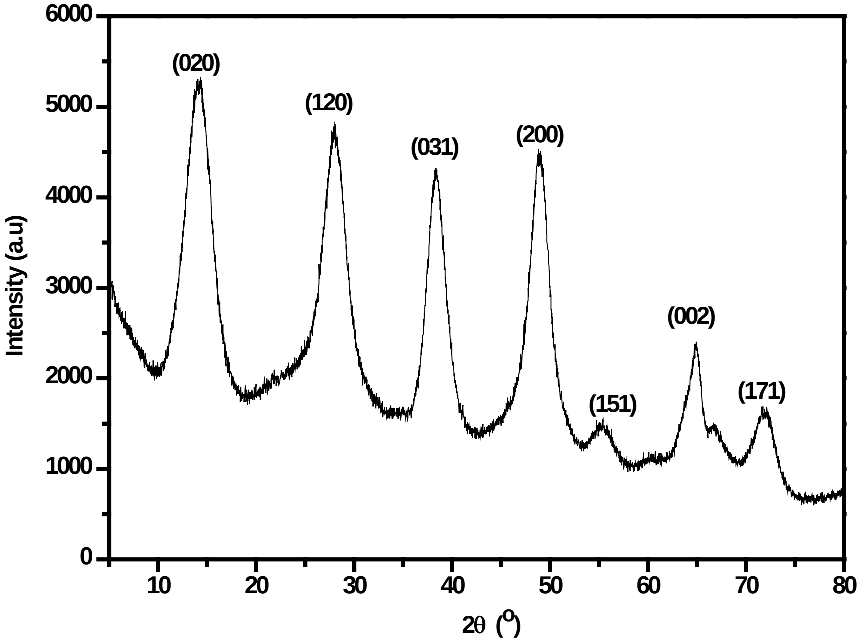

Fig. 1. XRD pattern of the sample

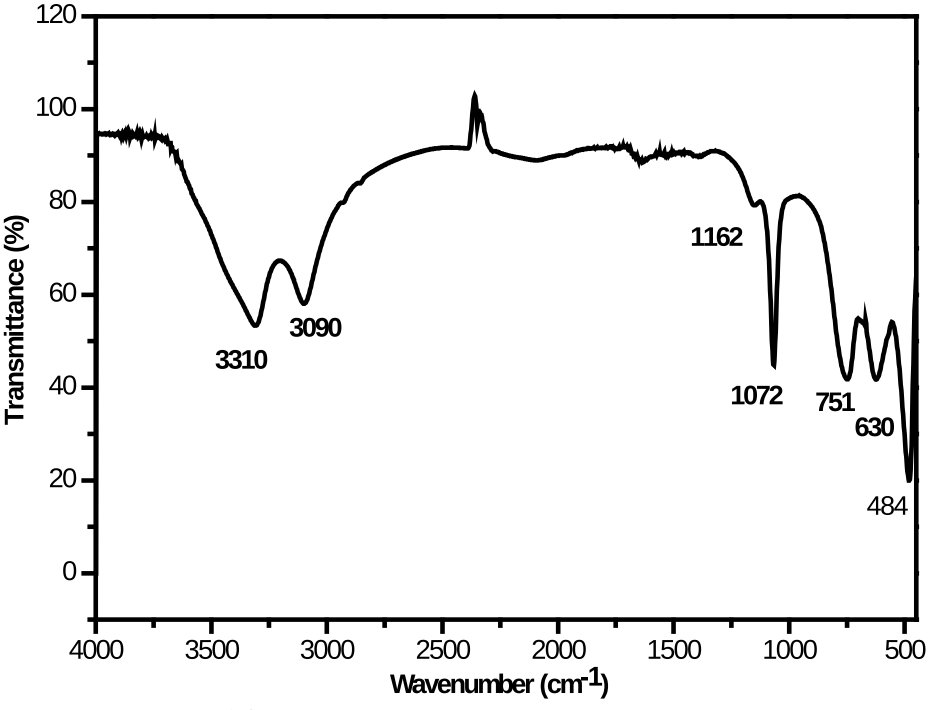

Fig. 2. FTIR spectrum of the sample

The textural properties of the catalyst γ-AlOOH were measured *via* a N_2 adsorption and desorption experiment. Figure 3a shows that the N_2 absorption and desorption isotherm of the γ-AlOOH was characteristic of a type IV isotherm with a type H_2 hysteresis loop above 0.4 P/P_0, which indicated mesopores were present. The pore size distribution (Fig. 3b) demonstrated that besides a wide pore size at 10.15 nm, the pore size of the γ-AlOOH was mainly centered at 2.87 nm. The detailed textural property of the γ-AlOOH can be seen in Table 1. The results were confirmed by its TEM. In Fig.

4, the γ-AlOOH consisted of a great number of irregular nanosheets with mean length of *ca*. 200 nm, and the surfaces of the nanosheets were not smooth and had a great number of small pores. Those numerous small pores in the γ-AlOOH were mainly about 2.87 nm in diameter. The effective accumulation of those nanosheets in forming the γ-AlOOH structure gave rise to a few large pores centered at 10.15 nm.

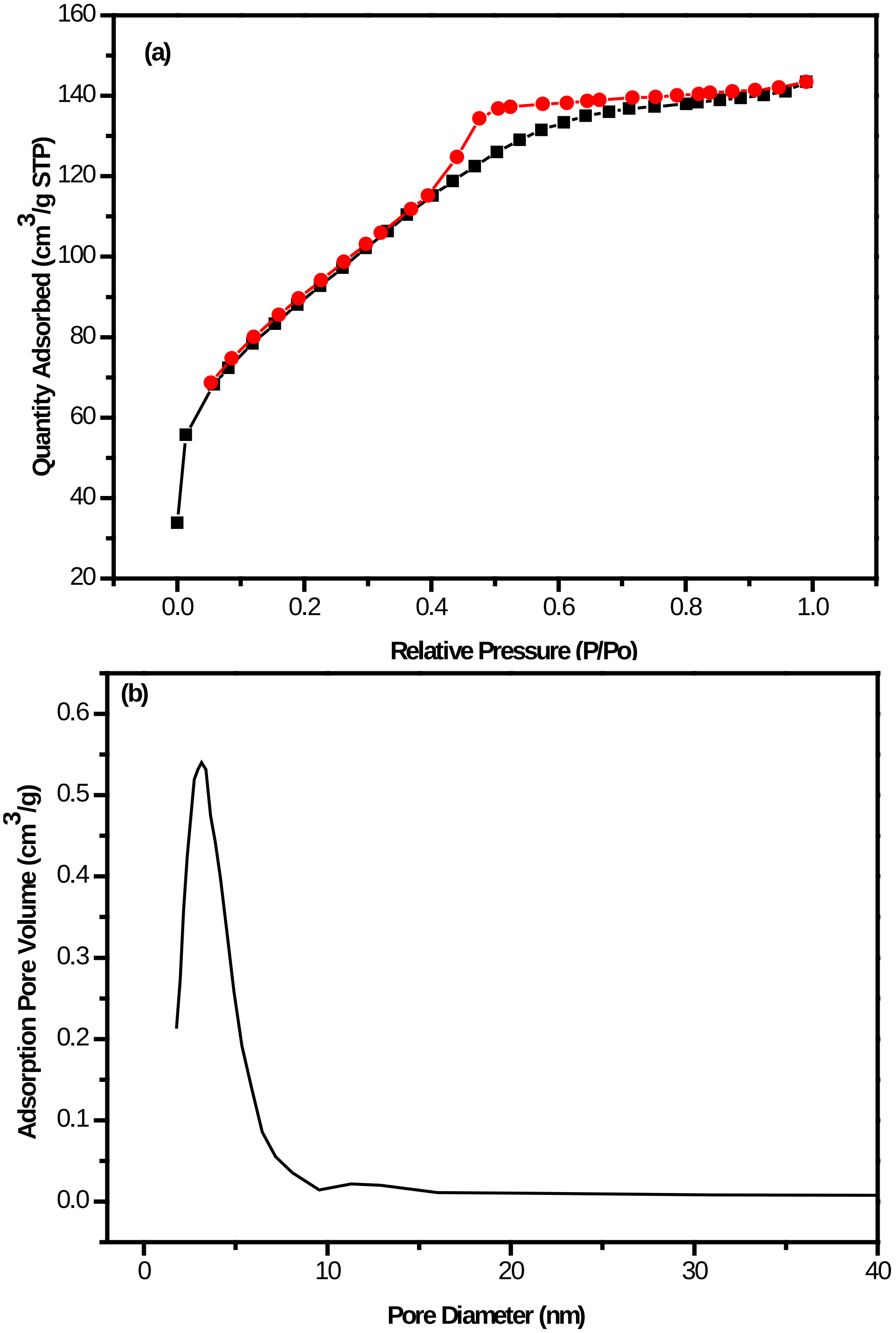

Fig. 3. N_2 adsorption and desorption isotherms (a) and pore size distribution (b) of the γ-AlOOH

Table 1. Textural and Acid Properties of the γ-AlOOH

BET Surface Area (m^2/g)	Pore Volume (cm^3/g)	Average Pore Size (nm)	Acid (Amount/μmol g^{-1})[a]	Acid Site (Density/Sites per nm^2)
316	0.22	3.10	83	0.21

[a]:Pyridine-IR

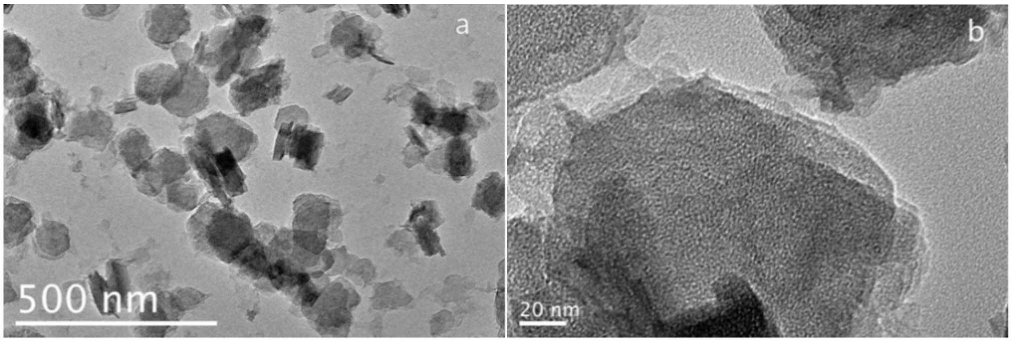

Fig. 4. TEM images of the γ-AlOOH with different scales: (a) 500 nm and (b) 20 nm

Thermogravimetric analysis of the γ-AlOOH was also performed under an air atmosphere. In Fig. 5, three stages of the weight loss were observed. Stage 1 was at 30 °C to 190 °C, which was attributed to the volatilization of the adsorbed waters on the surfaces of the γ-AlOOH (Sanchez-Valente *et al.* 2003). However, the weight loss was slight and less than 2%. Stage 2 ranged from 190 °C to 710 °C and was the main process of the weight loss up to 41%. The weight loss and the dehydration of γ-AlOOH into γ-Al_2O_3 occurred throughout the transformation (Chiche *et al.* 2008). Stage 3 occurred above 710 °C and was the crystal transformation from γ-Al_2O_3 into α-Al_2O_3 (Wang *et al.* 1998). The weight loss was also slight and could be neglected at less than 0.5%. The results indicated that if the reaction temperature was not higher than 190 °C, the γ-AlOOH was stabilized and would not be changed into another phase or decomposed.

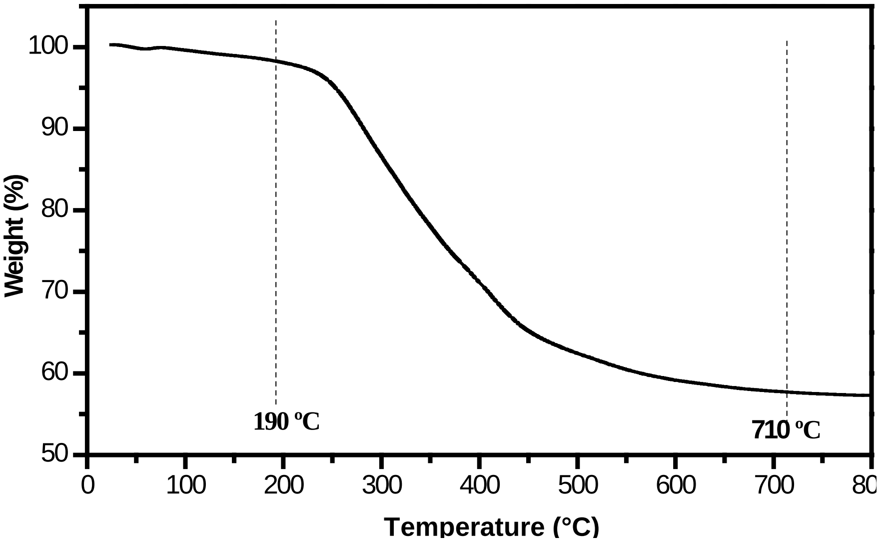

Fig. 5. TGA of the γ-AlOOH measured under air

Conversion of Glucose into HMF

To identify the products and calculate the carbon balance on the conversion of glucose, numerous technologies were adopted such as GC, HPLC, and GC-MS. Other than the HMF, some other compounds were found such as glucose, fructose, formic acid, levulinic acid, glyceraldehyde, and disaccharides. However, the yields of formic acid, levulinic acid, and glyceraldehyde were up to 6.5%, 4.5%, and 3.8%, respectively. The yields of other compounds were very low, less than 1%. The detailed information can be seen in Fig. 8. However, the conversion of glucose was 98.56% (Table 1), which meant that many other products were not detected. The result was consistent with those in numerous previous studies (Liu *et al.* 2015; Chen *et al.* 2016; Lopes *et al.* 2017). Although countless products were hard to be checked and identified in the present technologies, these could be also distinguished *via* the color change of the reaction from starting as colorless and turning black at the end. Hence, to clearly illustrate the changes of the components in the reaction, the products were classified into three types, which were HMF, others (glucose, fructose, formic acid, levulinic acid, glyceraldehyde, and disaccharides), and unidentified (difference of the total of the above two products based on mass balance). The detailed results are listed in Table 2.

Table 2. Conversion of Glucose into HMF Catalyzed by Different Catalysts

Entries	Catalysts	Catalyst Loading (mg)	HMF Yields (%)	Glucose Conversion (%)	Others Yields (%)	Unidentified Yields (%)
1	No catalyst	0	/	4.15	/	4.15
2	γ-AlOOH	100	61.24	98.56	10.23	27.09
3	HZSM-5	100	9.18	62.29	12.34	40.77
4	H_2SO_4[a]	327	21.47	84.47	18.24	44.76
5	HCl[b]	243	20.31	82.86	21.25	41.30
6	$CrCl_3$	100	34.50	85.45	11.26	39.69
7	$CrCl_2$	100	45.23	92.45	13.12	34.10

[a]: 25 wt% sulphuric acid; [b]: 25 wt% hydrochloric acid; reaction conditions were 0.1 g glucose, 2.5 g DMSO, 130 °C, and 3 h

Table 2 shows that γ-AlOOH had excellent catalytic activity for the conversion of glucose into HMF. Without any catalyst, HMF was hard to be detected, and the conversion of glucose was only 4.15% (Table 2). However, after the addition of 0.1 g γ-AlOOH into the reaction system, the yield of HMF was remarkably increased to 61.24%, and the conversion of glucose also increased to 98.56%. The results indicated the catalytic activity was principally attributable to the γ-AlOOH and the DMSO acted as the solvent to dissolve glucose and products on conversion of glucose. Furthermore, for the purpose of evaluating the catalytic performance of the γ-AlOOH, three kinds of catalysts were designed involved heterogeneous solid catalyst H-zeolite (HZSM-5), homogeneous Brønsted catalysts H_2SO_4 and HCl, homogeneous Lewis catalysts $CrCl_3$ and $CrCl_2$. Among these catalysts, the γ-AlOOH was the best catalyst with the highest yield and selectivity of HMF, suggesting that the γ-AlOOH not only can was efficient to catalyze glucose converted into HMF, but also effectively inhibited the side reaction from occurring. Among all the catalysts, only the γ-AlOOH produced 27.09% of the unidentified yields. While in other catalysts, the unidentified yields were above 34%.

However, from previous research (Delidovich and Palkovits 2016; Li *et al.* 2016; Graça *et al.* 2017), it can be inferred that the excellent catalytic activity on the conversion of glucose might have been attributed to its Lewis acid sites, because γ-AlOOH is a typical Lewis acid site catalyst (Wang *et al.* 1998; Sanchez-Valente *et al.* 2003; Chiche *et al.* 2008). Lewis acid sites can promote high isomerization of glucose into fructose and moderate dehydration of fructose into HMF. Figure 6 shows the Py-FTIR of the γ-AlOOH. In Fig. 6, only absorption peaks of Lewis acid sites appeared, which were at 1592 cm^{-1}, 1486 cm^{-1}, and 1450 cm^{-1}. No pyridine absorption peak of Brønsted acid sites (expected at 1540 cm^{-1}) occurred. The results showed that γ-AlOOH is a Lewis acid catalyst without the Brønsted acid sites. Furthermore, Table 3 lists the performances of the conversion of fructose into HMF using different catalysts. It should be noted that the conversion of fructose and HMF yield on the conversion of fructose were calculated as following equations:

$$\text{Fructose conversion}(\%) = 100\% - \frac{mole\ of\ fructose}{mole\ of\ starting\ fructose} \times 100\% \tag{3}$$

$$\text{HMF yield }(\%) = \frac{mole\ of\ HMF}{mole\ of\ starting\ fructose} \times 100\% \tag{4}$$

Table 3 shows that without any catalysts, only 15.88% HMF yield was obtained. Afterwards, when γ-AlOOH was added into the system, HMF yield was increased to 48.55%. From Table 2, a high HMF yield 61.24% was obtained on the conversion of glucose. However, when using other catalysts, such as HZSM-5, H_2SO_4, HCl, $CrCl_3$, the inverse results were obtained, low HMF yield from glucose and high HMF yield from fructose. All the results indicated that the γ-AlOOH has high isomerization of glucose into HMF and moderate dehydration of fructose into HMF.

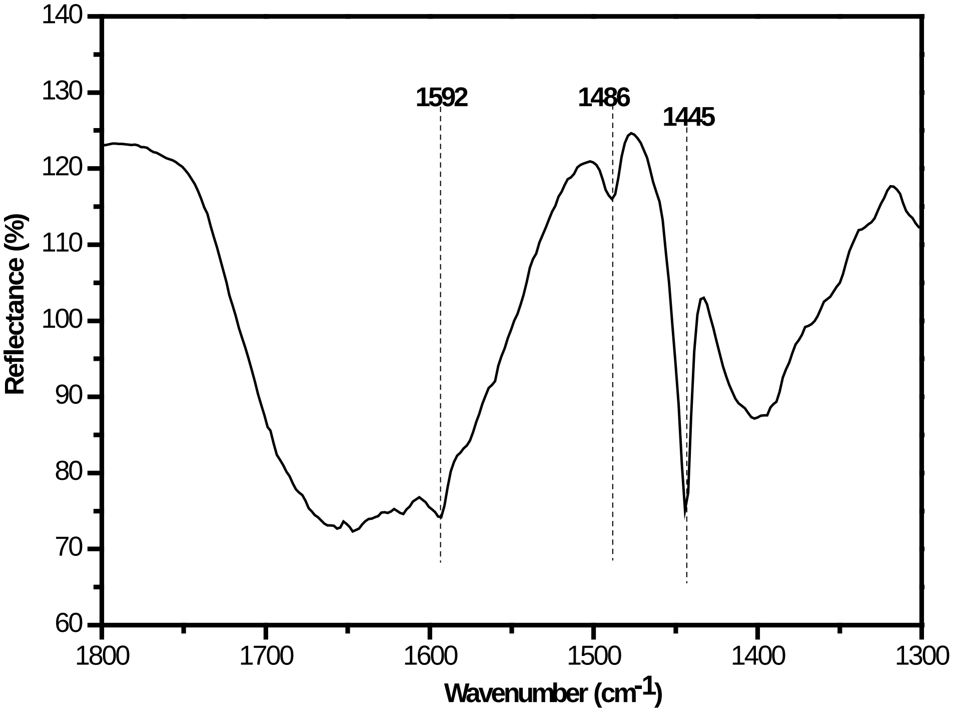

Fig. 6. Py-FTIR spectra of the γ-AlOOH

Table 3. Conversion of Fructose into HMF Under Different Catalysts

Entries	Catalysts	Catalyst Loading (mg)	HMF Yields (%)	Fructose Conversions (%)	Fructose Selectivity (%)
1	No catalyst	0	15.88	61.43	25.85
2	γ-AlOOH	100	48.55	82.36	58.64
3	HZSM-5	100	58.67	>99	59.26
4	H_2SO_4[a]	327	53.64	>99	54.18
5	HCl[b]	243	51.38	>99	51.38
6	$CrCl_3$	100	78.36	>99	79.15

[a]: 25 wt% sulphuric acid; [b]: 25 wt% hydrochloric acid; reaction conditions were 0.1 g glucose, 2.5 g DMSO, 130 °C, and 3 h

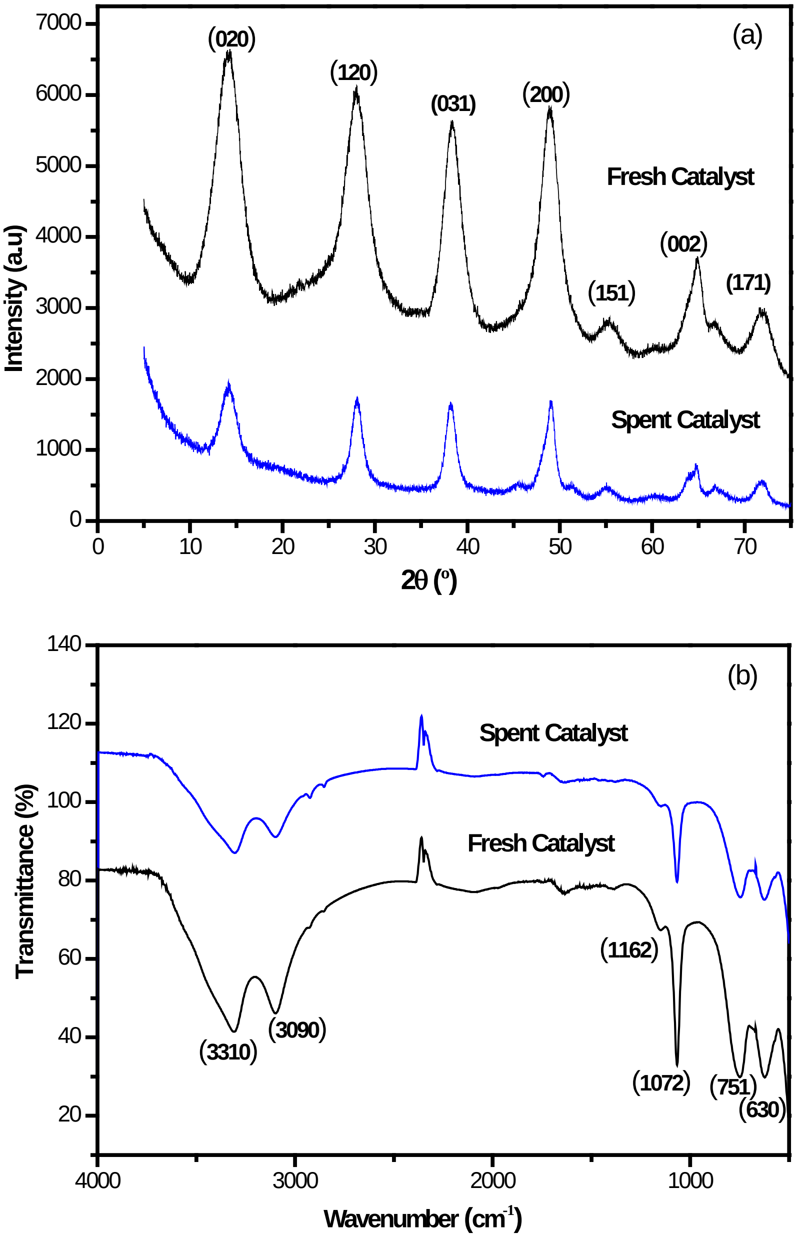

Fig. 7. XRD patterns (a) and FTIR spectra (b) of the γ-AlOOH before and after the reaction

Conversion of polysaccharides into HMF

To confirm the high hydrothermal stability of γ-AlOOH, the spent γ-AlOOH at 130 °C for 3 h was also checked by XRD and FTIR (Fig. 7). In both measurements, the characteristics of spent catalyst were the almost same with those of the fresh catalyst. All the results confirmed that γ-AlOOH was quite stable in the water-contained reaction system. Compared with the conversion of glucose into HMF, the degradation of polysaccharides into HMF would need more water, since besides the conversion of glucose into HMF, the reaction also involved hydrolysis of polysaccharides into glucose, which need extra addition of water. This meant that the γ-AlOOH might have been an effective catalyst to produce HMF from polysaccharides. To confirm the above hypothesis, the common polysaccharides maltose, sucrose, and cellulose were used as raw materials. The reaction procedure of the degradation of polysaccharides was the same as that of the conversion of glucose into HMF described earlier. The reaction parameters were changed to the following: 0.1 g γ-AlOOH; 0.1 g polysaccharides; 170 °C; 2.5 h, and certain amounts of solvents. The results of the HMF yields from maltose, sucrose, and microcrystalline cellulose are listed in Table 4. As shown, after 1.5 g H_2O was added into the reaction solvents of ionic liquid 1-butyl-3-methylimidazolium chloride and DMSO, all of the HMF yields increased considerably up to 53.63%, 62.15%, and 50.26% for maltose, sucrose, and microcrystalline cellulose, respectively. However, one noticeable difference of reaction parameters between the glucose and polysaccharides conversions was that the reaction solvents of polysaccharides conversion must contain ionic liquid 1-butyl-3-methylimidazolium chloride (IL). Without IL, HMF yields in the reaction were low and less than 3%. This might be ascribed to the fact that IL can react with -OH and β-oxygen ether bonds in the polysaccharides to form hydrogen bonds (Holm *et al.* 2013; Hu et al. 2013b; Wiredu and Amarasekara 2014).

Table 4. Conversion of Polysaccharides into HMF Catalyzed by Different Catalysts

Entries	Polysaccharides	Solvents	HMF Yields (%)
1	Maltose	2.0 g DMSO	3.56
2	Sucrose	2.0 g DMSO	11.26
3	Cellulose*	2.0 g DMSO	2.21
4	Maltose	2.0 g DMSO + 1.5 g H_2O	4.01
5	Sucrose	2.0 g DMSO + 1.5 g H_2O	10.36
6	Cellulose*	2.0 g DMSO + 1.5 g H_2O	2.25
7	Maltose	4.0 g IL[†] + 2.0 g DMSO	28.12
8	Sucrose	4.0 g IL[†] + 2.0 g DMSO	38.89
9	Cellulose*	4.0 g IL[†] + 2.0 g DMSO	22.35
10	Maltose	4.0 g IL[†] + 2.0 g DMSO + 1.5 g H_2O	53.63
11	Sucrose	4.0 g IL[†] + 2.0 g DMSO + 1.5 g H_2O	62.15
12	Cellulose*	4.0 g IL[†] + 2.0 g DMSO + 1.5 g H_2O	50.26

*: Cellulose was microcrystalline cellulose; [†]: IL was the ionic liquid 1-butyl-3-methylimi-dazolium chloride; reaction conditions were 0.1 g γ-AlOOH, 0.1 g carbohydrates, 170 °C, and 2.5 h

Effect of the solvents on the conversion of glucose into HMF

The solvent was a vital factor for the conversion of glucose into HMF. A total of seven common reagents, such as H_2O, DMSO, DMF, IL (1-butyl-3-methylimidazolium chloride), acetone, THF (tetrahydrofuran), i-PrOH (isopropanol), and their mixtures, were used as the solvents in the tests. The results are listed in Table 5. From entries 1 through 7, it was revealed that DMSO and IL were the best slovents among the single slovents. However, compared with 41.10% HMF yield in IL, the HMF yield in DMSO was up to 61.24 wt%. This result was different from the conclusions in a great number of previous works (Siankevich *et al.* 2014; Zhou *et al*. 2016; Paul and Chakraborty 2018), which showed that IL or IL mixtures were the best solvents for the conversion of glucose into HMF. To clearly understand the efffect of solvents on the synthesis of HMF from glucose, four kinds of their mixtures were adopted as the solvents, including IL-DMSO mixtures (entries 8 through 10), IL-other reagents mixtures (entries 11 through 15), DMSO-other reagents mixtures (entries 16 through 21), and other reagents mixtures (entries 22 through 24). It was demonstrated that among the solvents, the DMSO was the optimum solvent for the conversion of glucose into HMF, in which the HMF yield was up to 61.24%. Furthermore, it was found that in the mixtures with the increase of DMSO, the HMF yield increased immediately. For example, in the IL and IL-DMSO mixtures (entries 4 and 8 through 10), when the mass rates of DMSO and IL increased from 0:1 to 1:2 and 1:1 to 2:1, the HMF yield increased from 41.10% to 45.23%, 54.47%, and 56.68%. In the DMSO and DMSO-DMF (dimethyl formamide) mixtures (entries 3 and 16 through18), the mass rates of DMSO and DMF increased from 0:1 to 1:2 and 1:1 to 2:1, the HMF yield increased greatly from 2.81% to 33.07%, 45.23%, and 50.49%. The performance of DMSO might be attributed to its interactions with HMF via solation and high solubility for sugars (Dong *et al.* 2017; Morales *et al.* 2017; Dou *et al.* 2018).

Table 5. Effect of the Solvents on the Conversion of Glucose into HMF

Entry	Solvents	HMF Yields (%)	Glucose Conversions (%)	Entry	Solvents	HMF Yields (%)	Glucose Conversions (%)
1	H_2O	1.16	10.56	13	IL/Acetone (1:1)	24.87	87.32
2	DMSO	61.24	98.56	14	IL/i-PrOH (1:1)	20.42	85.23
3	DMF	4.81	20.36	15	IL/H_2O (1:1)	10.36	76.53
4	IL	41.10	96.85	16	DMF/DMSO (2:1)	33.07	87.32
5	Acetone	3.78	16.56	17	DMF/DMSO (1:1)	45.23	89.63
6	THF	8.53	45.65	18	DMF/DMSO (1:2)	50.49	98.13
7	i-PrOH	/	8.35	19	Acetone/DMSO (1:2)	44.95	93.36
8	IL/DMSO (2:1)	45.23	95.36	20	i-PrOH/DMSO (1:2)	32.07	85.69
9	IL/DMSO (1:1)	51.47	97.26	21	THF/DMSO (1:2)	48.31	93.56
10	IL/DMSO (1:2)	56.68	98.56	22	THF/DMF (1:2)	33.27	88.56
11	IL/DMF (1:1)	25.36	89.32	23	i-PrOH/DMF (1:2)	12.23	73.32
12	IL/THF (1:1)	30.12	93.53	24	Acetone/DMF (1:2)	18.07	81.32

Note: the rates in brackets of entries 8 to 24 were the mass rates of the before and after compounds and all total masses were 2.5 g; IL was 1-butyl-3-methylimidazolium chloride. Reaction condition: 0.1 g glucose;0.1g γ-AlOOH; 2.5 g DMSO; 130 °C, 3 h

Effect of the reaction duration on the conversion of glucose into HMF

To understand the possible reaction mechanism, the effect of reaction durations was investigated from 0.1 h to 10 h. Figure 8 shows that the amount of fructose was immediately up to the maximum of 8.5% at 0.1 h. Afterwards, with an increase in reaction times, the amount of fructose quickly decreased and approached to 0% at 4 h. This result indicated the fructose was an intermediate product during the conversion of glucose, and the reaction rate of dehydration of fructose into HMF was faster than that of the conversion of glucose into fructose.

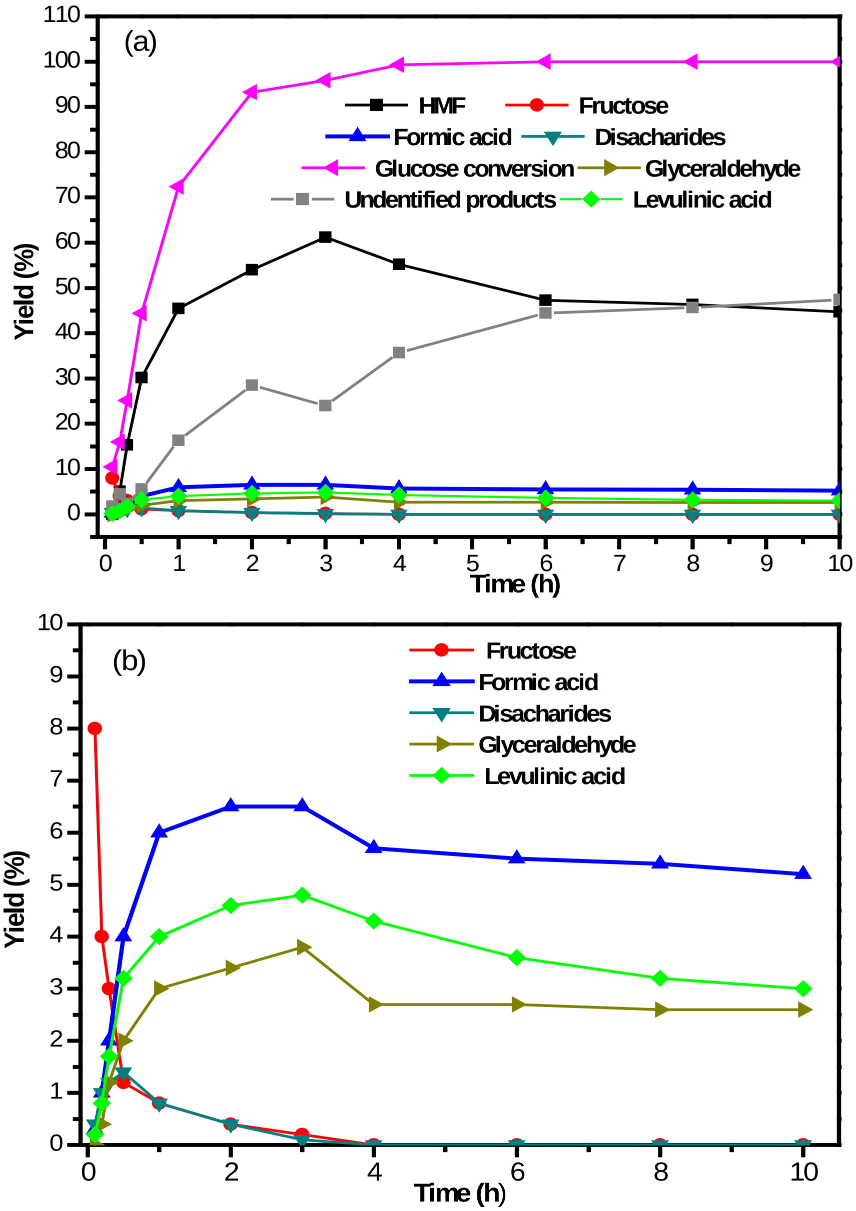

Fig. 8. Effect of reaction durations on conversion of glucose (a) and the yields of the major byproducts (b). Reaction condition: 0.1 g glucose;0.1g γ -AlOOH; 2.5 g DMSO; 130 °C

The quantity of the disaccharide, derived from the intermolecular condensation of optical isomers of glucoses, was minimal. The maximum quantity of disaccharide was not more than 1.5%. The amounts of the other three byproducts: glyceraldehyde, levulinic acid, and fromic acid, stemming from retrograde aldol condensations of fructose or glucose and the decomposition of HMF, were also low. All their maximum contents were less than 6.5%. Hence, the main byproducts were unidentified, such as soluble polymers and insoluble humins. Although the structures and formation mechanisms of the unidentified were not explicit, numerous works have argued that the unidentified compounds could be ascribed to the polymerization of HMF and intermediate dehydration products of fructose, in which HMF primarily was a crossing-linking agent (Lane *et al.* 2016; Martínez-Vargas *et al.* 2017; Morales *et al.* 2017; Zhang *et al.* 2017). According to the results and conclusions, the possible reaction mechanism was proposed and shown in Fig. 9.

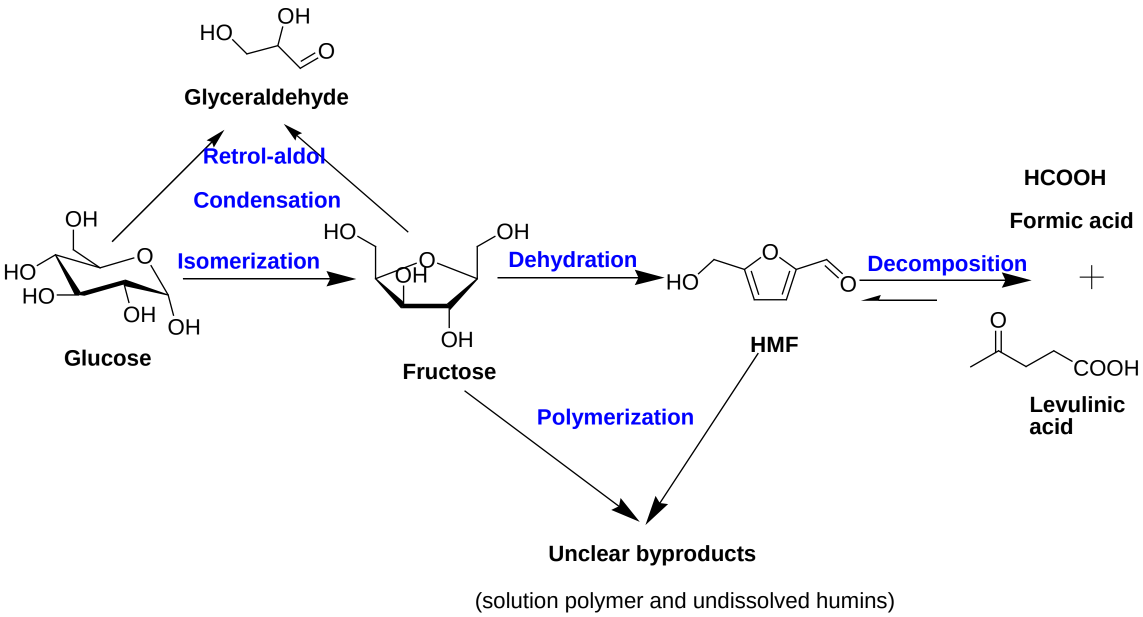

Fig. 9. Possible reaction process for the conversion of glucose

Furthermore, it was also discovered from Fig. 8 that the conversion of glucose increased with the increased reaction times. At 2 h, the conversion increased from 10.5% at 0.1 h to 93.26% at 2 h. Afterwards, the conversion slowly increased and gradually finished at 100%. However, the variation trend of HMF was different because the quantity levels first increased and then decreased. When the reaction time was not more than 3 h, the yield of HMF gradually increased and was up to the maximum of 61.24% at 3 h. However, when the reaction time was over 3 h, the HMF yield remarkably declined from 61.24% at 3 h to 55.21% at 4 h and 47.31% at 6 h, and gradually approached to 40%. Hence, the optimum reaction time was 3 h.

Effect of the catalytic loading and reaction temperature

The effects of the catalytic loading and reaction temperature were also investigated. Figure 10 reveals the changes of the reaction products on the variation of catalyst loadings at 130 °C for 3 h. When the catalyst loading was less than 0.1 g, the conversion of glucose increased with increased catalyst loading from 72.35% at 0.03 g to 95.86% at 0.10 g. However, a catalyst loading over 0.1 g resulted in the slow increased conversion of glucose and finished at 100%. The yield and selectivity of HMF were also varied with increased catalyst loading. When the catalyst loading was not more 0.1 g, the yield and selectivity of HMF increased with increased catalyst loading. When the catalyst loading was up to 0.1 g, the yield and selectivity of HMF were both at the maximum of 61.24% and 63.88%, respectively. Afterwards, further increase of the catalyst loading would lead the yield and selectivity of HMF to gradually decrease. The reason might be that in the reaction, the raw material glucose and intermediate product fructose would be adsorbed on the surface of the γ-AlOOH *via* the metal activity centers (Lewis acid sites) and hydroxyl/carbonyl moieties that are present in aldoses, and react to form the product HMF. When the catalyst loading was over 0.1 g, the excess metal activity centers (Lewis acid sites) would cause the HMF to react with other compounds such as glucose, fructose or to be decomposed into side products including formic acid and levulinic acid (Dimas-Rivera *et al.* 2014 and 2017).

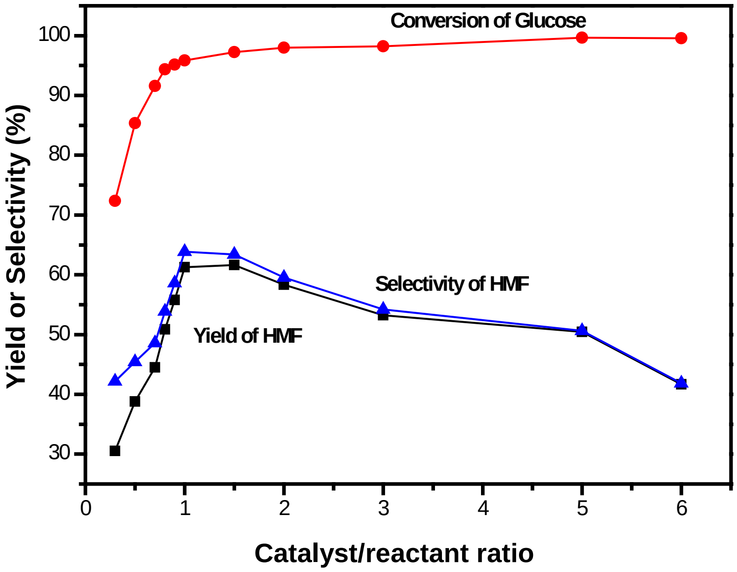

Fig. 10. Effect of the catalyst loading on the conversion of glucose. Reaction condition: 0.1 g glucose; 2.5 g DMSO; 130 °C; 3 h

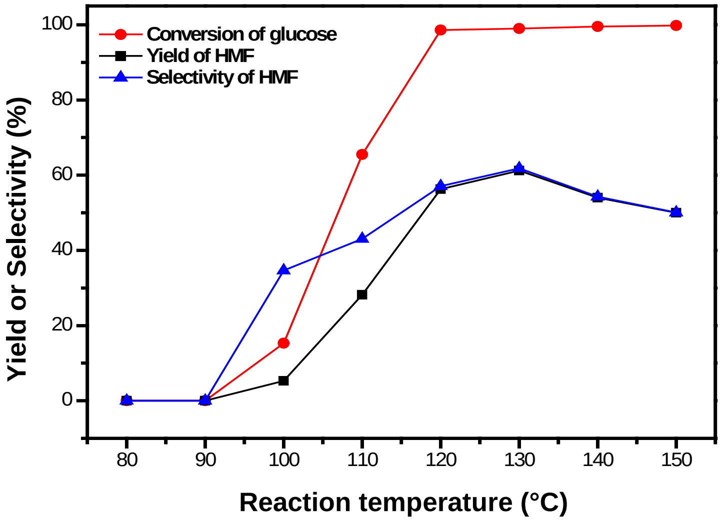

Fig. 11. Effect of the reaction temperature on the conversion of glucose. Reaction condition: 0.1 g glucose; 0.1g γ-AlOOH; 2.5 g DMSO; 3h

It was discovered that when the reaction temperature was lower than 100 °C, the conversion of glucose would not occur (Fig. 11). When reaction temperatures were more than 100 °C, the conversion rate of glucose noticeably increased. Especially in a range from 100 °C to 130 °C, the conversion of glucose greatly increased from 15.53% at 100 °C to 98.56% at 130 °C. Afterwards, further increase in temperature would trigger the conversion of glucose close to 100%. However, the variation of HMF did not follow the same trend. When the reaction temperature was over 100 °C, the HMF yield increased and gradually got close to its maximum at 61.24%. Afterwards, further increase in temperature would cause the HMF to quickly decline, which indicated an excessive reaction temperature and would promote countless side reactions to occur, which produced numerous side products.

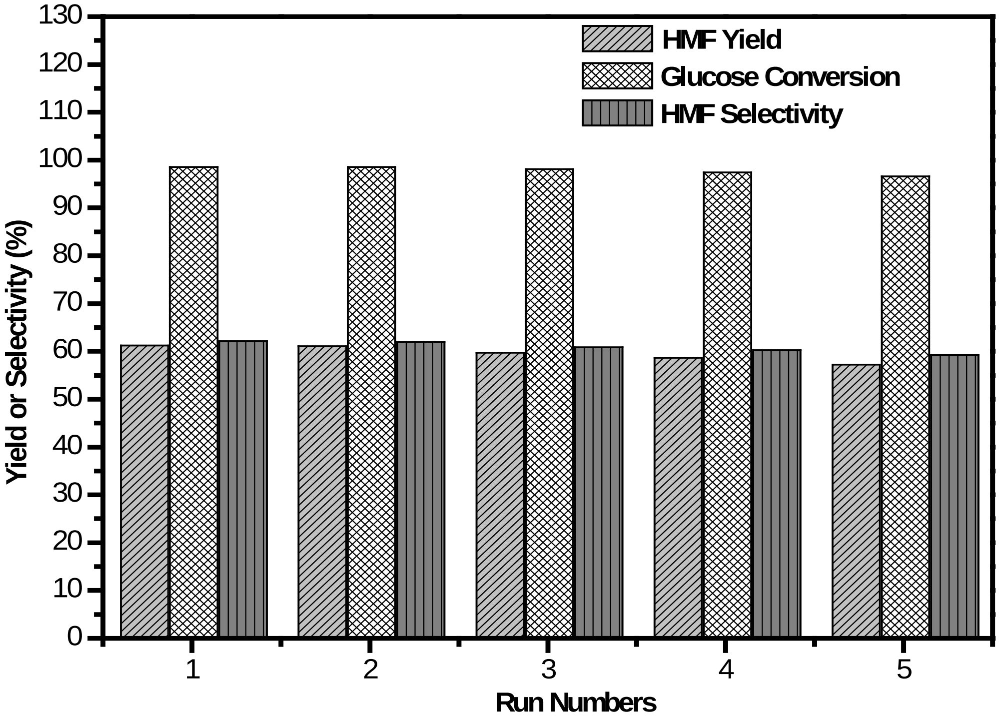

Fig. 12. Recycling experiments of the catalyst. Reaction condition: 0.1 g glucose;0.1g catalyst; 2.5 g DMSO; 130 °C, 3h

Recycling Experiments

Recycling experiments are an important factor in terms of the practical production of HMF. Figure 12 shows the results of recycling experiments. It was found that the catalyst γ-AlOOH possessed an effective and stable catalytic activity. After five reaction runs, the HMF yield and selectivity showed a slight decrease and remained at 57.23% and 59.25%, respectively.

CONCLUSIONS

1. A solid Lewis acid catalyst γ-AlOOH, a common industrial catalyst with easy preparation and low price, was used to catalyze glucose into HMF. The γ-AlOOH possessed high catalytic activity and good catalytic stability. A high HMF yield of

61.24% was obtained at the mild reaction condition of 130 °C for 3 h in the solvent DMSO.

2. More importantly, the catalyst γ-AlOOH could be reused several times without the loss of its important catalytic activities. After five reaction runs, an HMF yield of 57.23% and 59.25% selectivity were obtained.
3. HMF yields from other carbohydrates such as fructose (44.83%), cellulose (50.26%), Maltose (53.63%) and sucrose (62.15%) could be achieved using γ-AlOOH as a catalyst.

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