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Efficient Conversion of Glucose into 5-Hydroxymethylfurfural via a simple catalyst γ-AlOOH at a Mild Reaction Condition

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Abstract: A simple solid acid catalyst γ-AlOOH was employed to synthesize 5-hydroxymethylfurfural (HMF) from glucose in the dimethyl sulfoxide. Various reaction parameters, such as catalyst loading, temperature, reaction duration and solvent, were investigated. A high HMF yield of 61.24 % was obtained at the mild reaction condition of 130 °C for 3 h. More importantly, the catalyst γ-AlOOH could be reused for several times without the loss of its significant catalytic activities. After five reaction runs, a HMF yield about 57.23 % was obtained. In addition, the results demonstrated that the γ-AlOOH also had high catalytic activities on the degradation of other polysaccharides, like Maltose, Sucrose and Cellulose, into HMF using ionic liquid 1-butyl-3-methylimidazolium chloride, DMSO and a small amount of water as the reaction solvents. For instance, a high HMF yield of 50.26 % was obtained at 170 °C for 2.5 h on the decomposition of Cellulose.

Keywords: Heterogeneous Catalysis; Carbohydrates; HMF; Boehmite

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1. Introduction

The diminishing of petroleum sources, the growth of energy demand combined with growing concerns about global warming and environmental pollution had made the efficient utilization of renewable lignocellulosic biomass to be hot and significant in both academic study and industrial application [1, 2]. In the utilization of lignocellulosic biomass, the conversion of glucose, which is the most abundant component in lignocellulosic biomass and the most available and low-cost six carbon monosaccharide [3], into value-added chemicals is significantly important [4, 5]. Among the various value-added chemicals, HMF is considered as one of the "top 10" platform chemicals, which can be used as a raw materials to synthesize ocean of fine chemicals and other materials to replace or at least minimize the utilization of fossil- based products, such as 2,5-diformylfuran and 2,5-furandicarboxylic acid, 2,5- dimethyl- furan [6-8]. Recently, an review of the potential application of HMF has been summarized by Rosatella group [9].

Both homogeneous and heterogeneous catalysis were attempted to produce HMF from glucose. The used homogenous catalysts mainly contained metal salts, ionic liquid, mineral acid, inorganic and organic acid [10-14] .Compared with homogeneous catalysis, heterogeneous catalysis has been increasingly seem as the most promising one to convert glucose into HMF in terms of separation and recycling of catalysts [15,16]. In recent decades, numerous environmental benign heterogeneous solid acid catalysts, such as zeolite-based catalysts, Al_2O_3-based catalysts, SO_4^{2-}-based catalysts, doped catalyst, Nb-based catalysts, carbon-based catalysts, polymer-based catalysts and phosphate-based catalysts, have devolved to synthesis of HMF from glucose under various reactions systems, including ionic liquid system, organic solvents, biphasic system and water-contained systems [17-24]. Although relatively high HMF yields about 25-70 % were obtained in the catalytic systems, they tend to need high reaction temperatures about 160-200 ºC or complicate preparations of catalysts, which arouse the side reaction easily occur or hard to be applied in industry. Hence, it was necessary to seek a catalytic system used a simple catalyst under a mild reaction temperature.

It is generally argued that the process of producing HMF from glucose includes two continuous steps: isomerization of glucose into fructose and dehydration of fructose into HMF. And it It is generally argued the isomerization of glucose into fructose is the crucial and rate-determining step in the process of glucose conversion [25-27]. The isomerization of glucose into fructose can be more easily promoted by Lewis acid, bases and enzymes. Brønsted acid is more effective to improve fructose dehydrated into HMF [28, 29]. Moreover, it was also demonstrated that Lewis acid also own moderate catalytic activity on the dehydration of fructose into HMF [30, 31]. In addition, some solvents also owned some capacity to improve the dehydration of fructose into HMF, such as ionic liquids and aprotic organic solvents [32, 33]. Compared with the high price of ionic liquids, the aprotic organic solvents-DMSO is the low-cost and common used solvents. Therefore, we have reason to believe that using DMSO, and Lewis acid catalysts as the reaction system can be effective to promote the conversion of glucose into HMF.

It was known that Boehmite (γ-AlOOH) was one of Al_2O_3 precursors and one of typical Lewis acid catalysts. More importantly, it is easily prepared and own high hydrothermal stability [34-38]. The property is quite important, since water will be produced on the process of dehydration of fructose into HMF. The reaction results meant that the catalysts used on the conversion of glucose into HMF must own excellent high hydrothermal stability in order to keep catalytic stability. From the angle of γ-AlOOH with easy preparation and high hydrothermal stability, Takagaki et al. [39] used γ-AlOOH as the catalysts on the transformation of sugars (C_3-C_6 sugars) into fine chemicals, like dihydroxyacetone and glyceraldehyde. Although the aim of the reaction was not to produce HMF, ca. 18 % HMF yield was also detected on transformation of glucose. In a word, all the results indicated γ-AlOOH possesses the potential to efficiently and stably produce HMF from glucose.

In the work, γ-AlOOH were papered and used as catalysts to produce HMF from glucose assisted by DMSO as reaction solvent under the mild reaction condition of 130 °C. Various reaction parameters, including reaction durations, reaction temperature, catalytic loading, reaction solvent, were investigated. In addition, the conversions of other polysaccharides, like Maltose, Sucrose and Cellulose, into HMF were also investigated preliminarily.

2. Materials and Methods

2.1 Materials

HMF (99 %) was purchased from Aladdin Reagent Co. Ltd. (Shanghai China). All other reagents were analytic grades, purchased from Sinopharm Chemical Reagent Co. Ltd. and used as received.

2.2. Catalysts preparation

In a typical synthesis, 15 mmol $Al(NO_3)_3\cdot 9H_2O$ were added into 50 mL deionized water. Then, 30 mmol NH_4HCO_3 was slowly added under a violent stirring. After formation of a clear solution, 25 % ammonia water was slowly added until the pH was up to 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 cooled to the room temperature naturally. The product was collected through a centrifugation and washed several times with deionized waters. Finally, the sample was obtained by drying the product in a vacuum at 80 °C for 24 h.

2.3. Catalysts characterization

The phase structure of the sample was checked by Panalytical X-ray Power Diffraction (XRD) analysis with Cu-Kα radiation (λ=1.5406 Å). The data were recorded at 2θ range of 5-80°. The sample was further detected by Fourier transform infrared spectra (FT-IR, Nexusftir, Nieolet) in order to confirm its composition.

The textural property of the sample was investigated via nitrogen adsorption- desorption experiments measured by a Micromeritics ASAP 2020 system. The specific surface areas and pore size distributions of the samples were calculated using Brunauer-Emmett-Teller (BET) equation and Barrett-Joyner-Halenda (BJH) method respectively. The morphology and microstructure of the samples were further observed by the transmission electron microscopy (TEM, JEM-2100UHR, JEOL). The thermal gravimetric analyses (TGA) of the samples were carried out at a heating rate of 10 °C /min under Air-atmosphere (Model: SDT Q600).

Lewis and Brønsted acidic sites were investigated via FT-IR pyridine adsorption technique (Py-FTIR, Nicolet, USA) [40]. IR spectra recorded at a resolution of 4 cm-1ine the range of 1700-1400 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 coefficients, 2.22 cm $mmol^{-1}$ [41, 42].

2.4. Typical procedure of HMF from glucose

The experiments were carried out in the tube of 18 mm ×180 mm with a lid. In the typical process, 100 mg glucose and 100 mg catalyst were added into 2.5 g DMSO under vigorous stirring. After forming a homogeneous solution, the mixtures were heated at 130 °C for 3 h under an 800 rpm magnetic stirring. Afterwards, the reaction mixtures were quickly cooled to the room temperature by an addition of 20 ml cold deionized water. Then, the forming mixtures were centrifuged at 10000 rpm for 5 min and weighed. The above clear liquid was collected. After diluted 150-200 times by the deionized water, the solution was sent to be analyzed.

2.5. Analysis

HMF was detected by High Performance Liquid Chromatography (HPLC, Agilent 1200) equipped with an ultraviolet detector (UV-9600, Beijing Purkinje General Instrument CO. Ltd., China) at the ultraviolet wavelength of 284 nm and the External Standard Method. Glucose and other carbohydrates, such as fructose, disaccharides, were also checked by High Performance Liquid Chromatography (HPLC, Agilent 1200) outfitted with a refractive index with an ion exclusion column (300 mm × 7.8 mm, Aminex HPX-87H) at 60 °C. The other compounds were detected by the Gas Chromatography (GC1690, Jiedao, China) and the External Standard Method. The yield of HMF and conversion of glucose were calculated according to the following equations:

Glucose conversion=100 %-(mole of glucose in the product) / (mole of starting glucose)×100%

HMF yield =(mole of HMF)/(mole of starting glucose)×100%.

3. Results and Discussion

3.1. Characterization of the catalyst

The phase structure of the sample was checked by power XRD (shown in the Fig.1). All its diffraction peaks can be assigned to an orthorhombic γ-AlOOH (JCPDS Card 021-1307). No peaks from other phases were observed, indicated the high purity of the catalyst. Further evidence on the formation of γ-AlOOH was derived from the result on its FT-IR. In the Fig.2, it can be seen that the bands at 3310, 3090, 1072 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. While, the bands at 751, 630, and 484 cm^{-1} belonged to the vibration mode of AlO_6. All the results revealed that γ-AlOOH was successfully prepared.

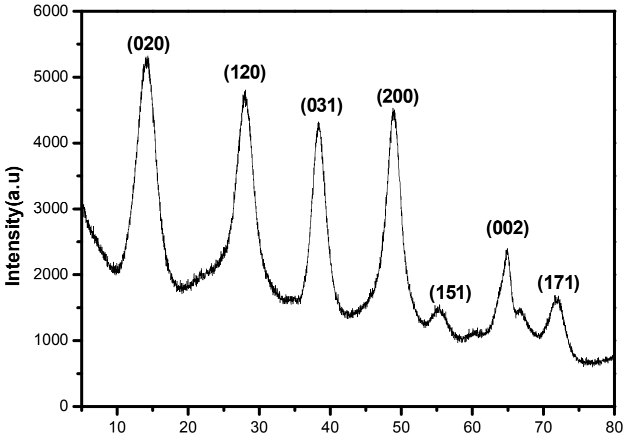

Fig. 1 XRD pattern of the sample

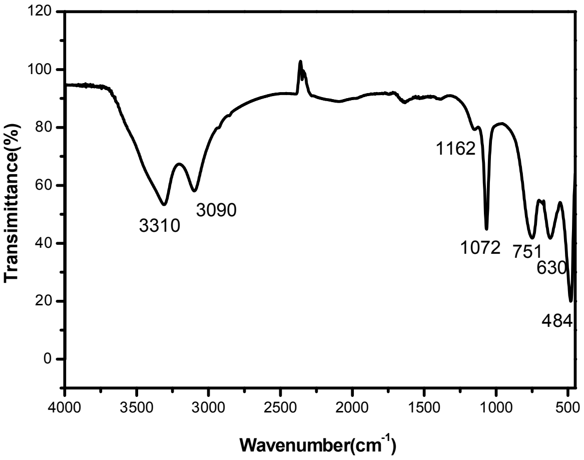

Fig. 2. FT-IR spectrum of the sample

The textural property of the catalyst γ-AlOOH was measured by N_2 adsorption and desorption experiment. In the Fig.3, it can be seen 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/P0, indicating there existed meso-pores. And its pore size distribution (the inset) 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 the Table 1. The results were confirmed by its TEM. In the Fig. 4, the γ-AlOOH was composed by a great number of irregular nanosheets. After a carefully observation of its high-magnification TEM image, it was discovered that the surfaces of the nanosheets were not smooth and have a great number of small pores.

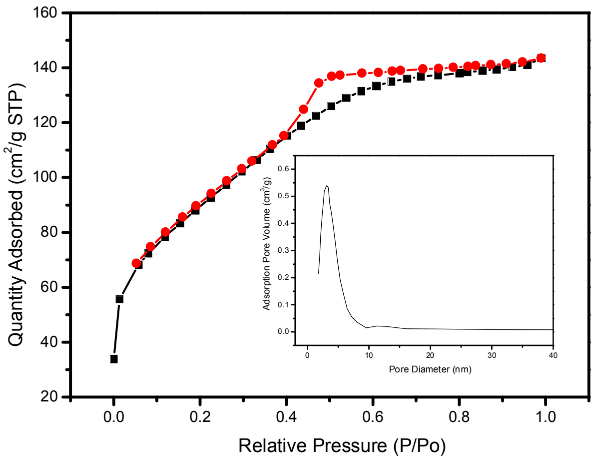

Fig. 3. N_2 adsorption and desorption isotherms and Pore size distribution (inset) of the γ-AlOOH

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 [a] /umol g^{-1}	Acid site density/sites per nm^2
316	0.22	3.10	83	0.21

a: Pyridine-IR

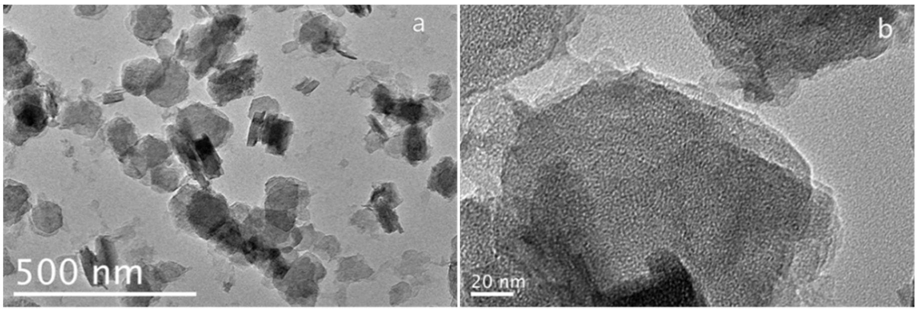

Fig.4. TEM images of the γ-AlOOH with low (a) and high magnification (b)

Thermogravimetric analysis of the γ-AlOOH was also investigated under the air atmosphere. In the Fig.5, three stages of the weight loss were observed. Stage 1 was 30-190 °C, attributed to the volatilization of the adsorbed waters on the surfaces of the γ-AlOOH [34]. But the weight loss was slight, less than 2 %. Stage 2 ranged from 190 to 710 °C was the main process of the weight loss, up to 41 %. The weight loss was to the transformation from the dehydration of γ-AlOOH into γ-Al_2O_3 [35]. Stage 3 above 710 °C was to the crystal transformation from γ-Al_2O_3 into α-Al_2O_3 [37]. The weight loss was also very slight and can be neglected, less than 0.5 %. The results indicated that if only the reaction temperature was not high than 190 °C, the γ-AlOOH was stabilized and wouldn't be changed into other phase or decomposed.

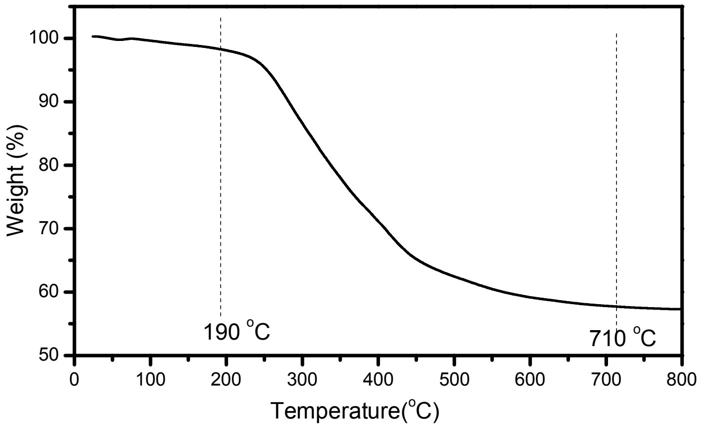

Fig. 5. Thermogravimetric analysis of the γ-AlOOH under air condition

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 GC-MS. Besides the HMF, some other compounds were found, such as glucose, fructose, formic acid, levulinic acid, glyceraldehyde and disaccharides. However, except that 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 the Fig.8. However, in the work, the conversion of glucose was 98.56 % (Entry 2 of Table 1), which meant that many other byproducts were not detected. The result was well consisted with numerous previous researches [23, 24]. Although countless byproducts were hard to be checked and identified in the present technologies, these could be also proved via the color change of the reaction from colorless at begin to black at end. Hence, in order to clearly illustrate the changes of the components in the reaction, the products were classified into four types in the work, which were HMF, Glucose, Others (glucose, fructose, formic acid, levulinic acid, glyceraldehyde and disaccharides), and Unidentified. The detailed results were listed in Table 2. It should to be noted that the yield of Unidentified was equal to the difference of the conversion of glucose minus the yields of HMF and Others.

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 cata.	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}	140	21.47	84.47	18.24	44.76
5	HCl^b	111	20.31	82.86	21.25	41.3
6	$CrCl_3$	100	34.50	85.45	11.26	39.69
7	$CrCl_2$	100	45.23	92.45	13.12	34.1

a: 25 wt % sulphuric acid; b: 25 wt % hydrochloric acid

The reaction condition: 0.1 g glucose; 2.5 g DMSO; 130 °C; 3 h.

From the Table 2, it can be seen 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 to 4.15 % (Entry 1). However, after adding 0.1 g γ-AlOOH into the reaction system, the yield of HMF remarkably increased into 61.24 %, the conversion of glucose also tremendously increased to 98.56 %. The results indicated the catalytic activity was principally stemmed from the γ-AlOOH and the DMSO was chiefly acted as the solvent for dissolve glucose and products. Furthermore, on the purpose of evaluating the catalytic performance of the γ-AlOOH, three kinds of catalysts were designed like heterogeneous solid catalyst HZSM-5, homogeneous Bronsted catalysts H_2SO_4, HCl and 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 be efficient to catalyze glucose converted into HMF, but also can effectively inhibit the side reaction occur. Among all the catalysts, only the γ-AlOOH produced 27.09 % of the Unidentified yields. While in others catalysts, the Unidentified yields were not less than 34 %.

However, from many previous [25-30], it can be inferred that the excellent catalytic activity on the conversion of glucose might be attributed to its Lewis acid sites, since γ-AlOOH was typical Lewis acid sites catalyst [34-38] and Lewis acid sites own high isomerization of glucose into fructose and moderate dehydration of fructose into HMF. Fig. 6 shows the pyridine adsorbed Fourier transform infrared spectra (Py-FTIR) of the γ-AlOOH. In the Fig.6, there appeared only absorption peaks of Lewis acid sites, which were 1592, 1486 and 1450 cm^{-1}. No pyridine absorption peaks of

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Brønsted acid sites (at 1540 cm^{-1}) were occurred. The results proved that γ-AlOOH was a Lewis acid catalyst without Brønsted acid sites. Furthermore, Table 3 listed the performances of the conversion of fructose into HMF using different catalysts. It can be seen that without any catalysts, only 15.88 % HMF yield was obtained. Afterwards, when γ-AlOOH was added into the system, HMF yield was increased into 48.55 %, indicated the γ-AlOOH has moderate dehydrate of fructose into HMF. While, based on the reaction contained two continuous steps of isomerization of glucose into fructose (Rate determining step) and dehydration of fructose into HMF, and the high HMF yield (61.24 %) on the conversion of glucose at the same reaction condition, it meant that the γ-AlOOH owned excellent isomerization of glucose into fructose.

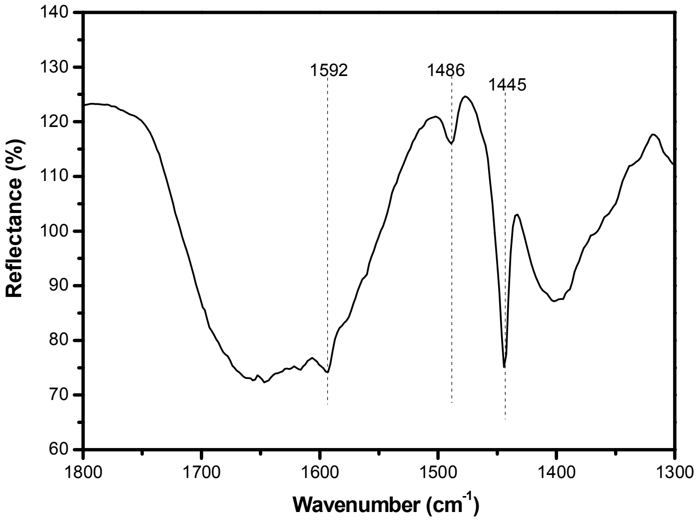


Fig. 6. Py-FTIR spectra of the γ-AlOOH

Table 3. Conversion of fructose into HMF under different catalysts

Entries	Catalysts	Catalyst loading (mg)	HMF Yields (%)	Fructose Conversions (%)
1	No catalyst	0	15.88	61.43
2	γ-AlOOH	100	48.55	82.36

The reaction condition: 0.1 g fructose; 2.5 g DMSO; 130 °C; 3 h.

3.3. Conversion of polysaccharides into HMF

In order 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 FT-IR (shown in Fig.7). In both measurements, the conditions of spent catalyst were almost same with that of the fresh catalyst. Just the full width at half maximum (FWHM) of the spent γ-AlOOH was slightly narrower than that of the fresh γ-AlOOH, indicated that after the reaction at 130 °C for 3 h, the crystalline grain of the γ-AlOOH was grown up slightly. 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 need more water than that of the conversion of glucose into HMF, since the reaction still contained the hydrolysis of polysaccharides, besides the isomerization of glucose and dehydration of fructose, which suggests that the γ-AlOOH possibly might be one of effective catalyst to produce HMF from the polysaccharides, a raw reaction material to produce HMF with of more cheap, extensive and close to biomass. In order to verify the supposal, the common polysaccharides, Maltose, Sucrose and Cellulose, were used raw materials. The reaction procedure of the degradation of polysaccharides was the same with that of conversion of glucose into HMF in section 2.4. Just the reaction parameters were change as following: 0.1 g γ-AlOOH; 0.1 g polysaccharides; 170 °C; 2.5 h, different solvents. The results of HMF yields from Maltose, Sucrose and Microcrystalline Cellulose were listed in Table 4. It can be seen that after added 1.5 g H2O into the reaction solvents ionic liquid 1-butyl-3-methylimidazolium chloride and DMSO, all the HMF yield were increased significantly, up to 53.63 %, 62.15 % and 50.26 %, corresponding to Maltose, Sucrose and Microcrystalline Cellulose respectively. The results confirmed our above supposal that the γ-AlOOH was one of effective catalyst to produce HMF from the polysaccharides. However, one of significant difference from the conversion of glucose into HMF was that the reaction solvents must contain ionic liquid 1-butyl-3-methylimidazolium chloride. Without IL, HMF yields in all reaction raw materials were very low, not more than 3 %. This might be ascribed to the dissolution of polysaccharides in IL. In many previous works, they demonstrated that ionic liquids, including 1-butyl-3-methylimidazolium chloride, own high dissolution of cellulose, since it can react with -OH and β-oxygen ether bonds in the polysaccharides to form hydrogen bonds [43-45]. But the detailed reason, the effect of reaction condition on the conversion of polysaccharides into HMF, such as reaction temperature, reaction duration, catalyst load, solvents, H_2O and other parameters, were studied in our future work.

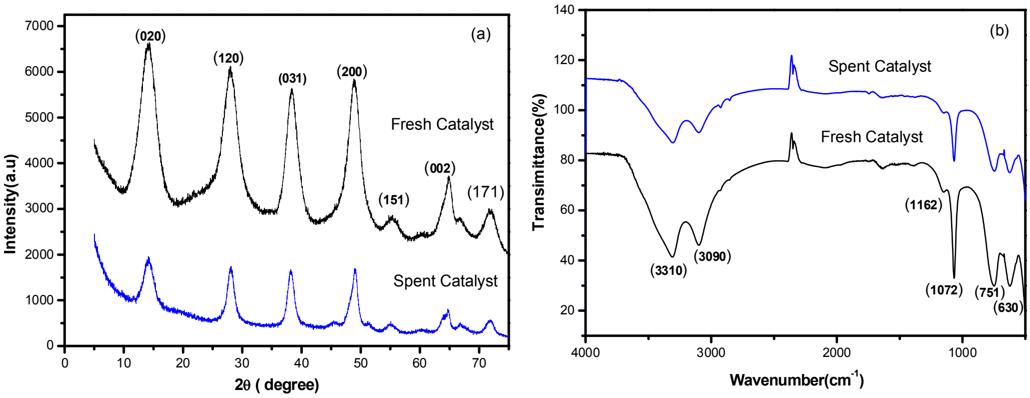


Fig. 7. XRD patterns (a) and FT-IR spectra (b) of the γ-AlOOH before and after the reaction

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 the microcrystalline cellulose

: IL was the ionic liquid 1-butyl-3-methylimidazolium chloride

The reaction condition: 0.1 g γ-AlOOH; 0.1 g Carbohydrates; 170 °C; 2.5 h.

3.4. Effect of the solvents on the conversion of glucose into HMF

The solvent was a vital factor for the conversion of glucose into HMF. Seven common reagents, such as H_2O, DMSO, DMF, IL (1-butyl-3-methylimidazolium chloride), Acetone, THF and i-PrOH, and their mixtures were used as the solvents in the tests. The results were listed in the Table 5. From Entries 1-7, it was revealed that DMSO and IL were the best solvents among the signal solvents. However, compared with 41.10 % HMF yield in IL, the HMF yield in DMSO was up to 61.24 %. The result was different from the conclusions in a great number of previous works [51-53], which showed that IL or IL mixtures were the best solvents for the conversion of glucose into HMF. In order to obviously understand the effect of solvents on synthesis of HMF from glucose, four kinds of their mixtures were adopted as the solvents, including IL-DMSO mixtures (Entries 8-10), IL-other reagents mixtures (Entries 11-15), DMSO-other reagents mixtures (Entries 16-21) and other reagents mixtures (Entries 22-24). It was demonstrated that that among all those solvents, the DMSO was the optimum solvent on 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 was mounted immediately. For examples, in the IL and IL-DMSO mixtures (Entries 4,8-10), when the mass rates of DMSO and IL increased from 0:1 into 1:2, 1:1 and 2:1, the HMF yield increased from 41.10 % into 45.23 %, 54.47 % and 56.68 %. And in the DMSO and DMSO-DMF mixtures (Entries 3, 16-18), the mass rates of DMSO and DMF increased from 0:1 into 1:2, 1:1 and 2:1, the HMF yield soared from 2.81 % into 33.07 %, 45.23 % and 50.49 %. The performance of DMSO might be attributed to their strong polarities [33]. Firstly, it can acts as a promoter or catalyst in the conversion of sugars. Secondly, it interacts strongly with HMF through solvation, and thereby restricts the contact of HMF with intermediates and water molecules, preventing the undesired side reactions. Finally, owing to its high solubility for sugars including starch, and the product HMF, it is possible to conduct reaction even at high substrate concentrations [54-56].

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

En.	Solvents	HMF Yields (%)	Glucose Conversion (%)	En.	Solvents	HMF Yields (%)	Glucose Conversion (%)
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 8-24 were that mass rates of before and after compounds and all total masses were 2.5g; IL was 1-butyl-3-methylimidazolium chloride.

The reaction condition: 0.1 g glucose; 0.1g glucose; 2.5 g DMSO; 130 °C; 3 h.

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

In order to understand the possible reaction mechanism, the effect of reaction durations was investigated from 0.1h to 10 h. From the Fig.8, it can be seen that the amount of fructose was immediately up to the maximum of 8.5% at 0.1 h. Afterwards, with the increase of reaction times, the number of fructose decreased quickly and significantly and closed to 0 % at 4 h. The result indicated the fructose was intermediate products on the conversion of glucose, and the reaction rate of dehydration of fructose into HMF was much faster than that of conversion of glucose into fructose. The quantity of disaccharide, derived from the intermolecular condensation of optical isomers of glucoses, was very few. The maximum quantity of disaccharide was not more than 1.5 %. The amounts of other three byproducts-Glyceraldehyde, levulinic acid and Formic acid, stemmed from retrograde aldol condensations of fructose or glucose and decomposition of HMF respectively, were also not much high. All their maximum contents were not more than 6.5 %. Hence, the main byproducts were the Unidentified, such as soluble polymers and insoluble humins. Although the structures and formation mechanisms of the Unidentified were not explicit, numerous works [49, 50] argued that the Unidentified compounds were ascribed to the polymerization of HMF and intermediate dehydration products of fructose, in which HMF primarily played as crossing-linking agents. According to the results and conclusions, the possible reaction mechanism was proposed and showed in the Sch. 1.

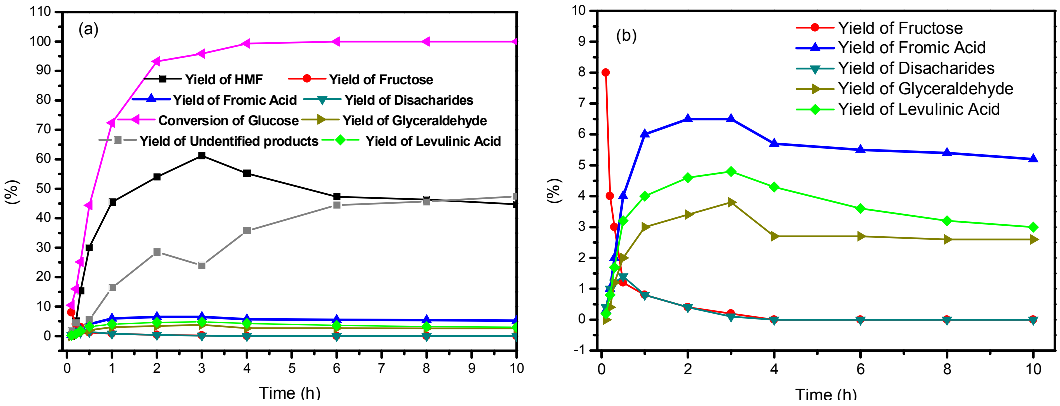
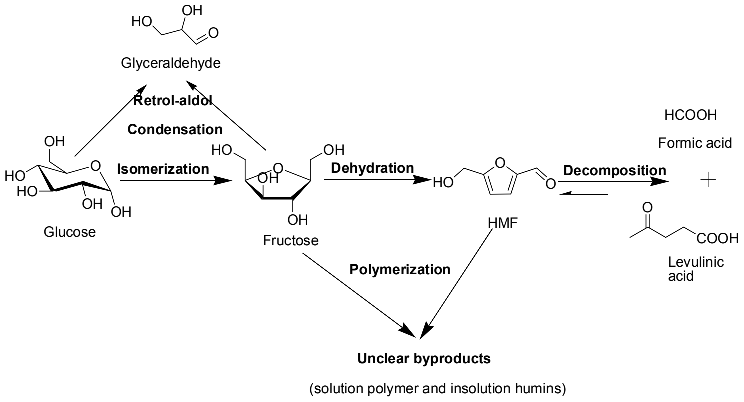


Fig.8. Effect of reaction durations on conversion of glucose (a) and the yields of the major byproducts (b)



Sch. 1 Possible reaction process for the conversion of glucose

Furthermore, it was also discovered from the Fig.8 that the conversion of glucose increased with the mounting of reaction times. In the starting 2 h, the conversion increased greatly from 10.5 % at 0.1 h to 93.26% at 2 h. Afterwards, the conversion increased slowly and gradually closed to 100 %. However, the variation trend of HMF was different; whose quantity firstly increased then decreased. When the reaction time was not more than 3 h, the yield of HMF mounted gradually and was up to the maximum at 3 h of 61.24 %. But when the reaction time was over 3 h, the yield of HMF was declined remarkably from 61.24 % at 3 h to 55.21 % at 4 h and 47.31 % at 6 h and gradually tended to be a steady value of 40 %. Hence, the optimum reaction time was 3 h.

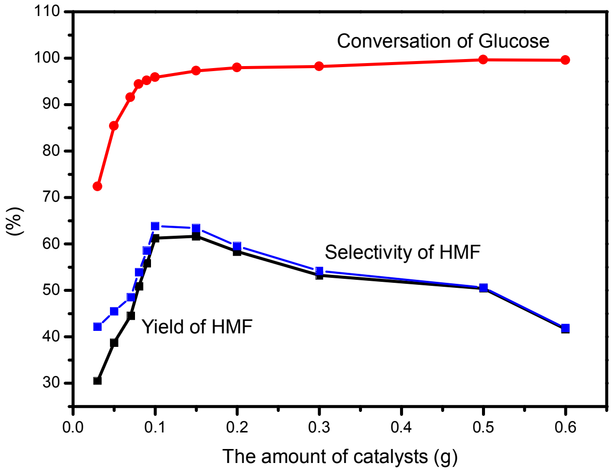


Fig.9. Effect of the catalyst loading on the conversion of glucose

3.6. Effect of the catalytic loading and reaction temperature

Effect of the catalytic loading and reaction temperature were also investigated. Fig.9 revealed the changes of the reaction products on the variation of catalyst loadings at 130 °C for 3 h. It was found from Fig.9 that when the catalyst loading was not more than 0.1 g, the conversion of glucose soared with the increase of catalyst loading from 72.35 % at 0.03 g to 95.86 % at 0.10 g. However, after the catalyst loading was over 0.1 g, the conversion of glucose increased slowly and closed to 100 %. The yield and selectivity of HMF were also varied with the increase of catalyst loading. When the catalyst loading was not more 0.1 g, the yield and selectivity of HMF was soared with the increase of catalyst loading. When the catalyst loading was to 0.1g, the yield and selectivity of HMF were both to the maximum, up to 61.24 % and 63.88 %. Afterwards, further increase of catalyst loading would lead the yield and selectivity of HMF to decrease gradually. The results indicated when the catalyst loading was over 0.1 g, the excessive catalyst would arouse more side reaction occur, such as decomposition of HMF or polymerizations of HMF and glucose, and produced countless undesired byproducts, such as soluble oligosaccharides and insoluble oligomers.

It was discovered when the reaction temperature was low than 100 °C, the conversion of glucose was nearly not happening. No HMF was detected. And when reaction temperature was more than 100 °C, the conversion rate of glucose increased significantly. Especially at range from 100 to 130 °C, the conversion of glucose was skyrocketed from 15.53 % at 100 ºC to 98.56 % at 130 °C. Afterwards, further increase of temperature would trigger the conversion of glucose close to 100 %. However, the variation of HMF didn't follow the trend. When the reaction temperature was over 100 °C, HMF yield was soared and gradually closed to the maximum, up to 61.24 %. Afterwards, further increase of temperature would arouse HMF decline quickly, which indicated excessive reaction temperature would trigger countless sides reactions occur and produced numerous side products.

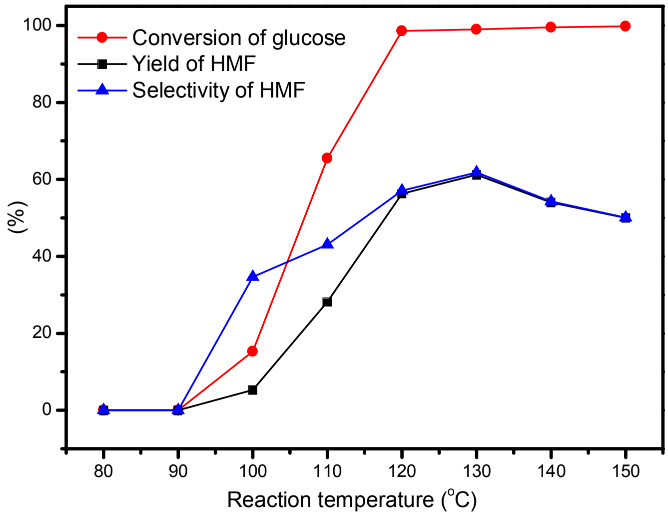


Fig.10. Effect of the reaction temperature on the conversion of glucose

3.7. *Recycling Experiments*

Recycling experiments are an important factor in terms of the practical production of HMF. Fig.11 shows the results of recycling experiments. It was found that the catalyst γ-AlOOH owned a well stabile catalytic activity. After five reaction runs, HMF yield and selectivity were only a slight decrease, and kept at 57.23 % and 59.25 %, respectively.

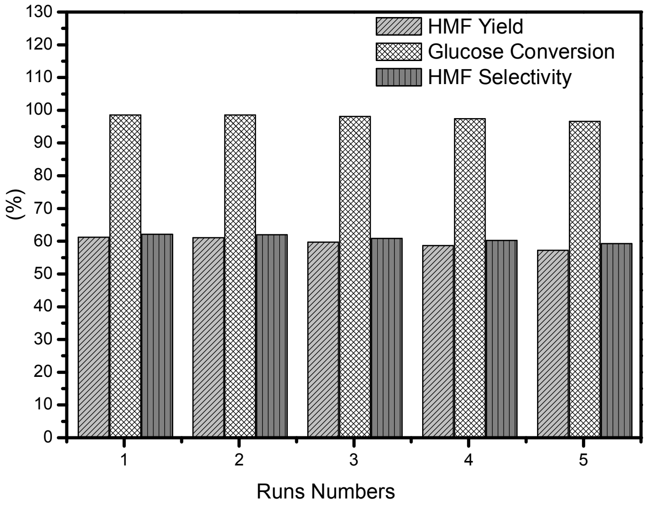


Fig. 11 Recycling experiments of the catalyst

4. Conclusions

In the work, a simple solid catalyst γ-AlOOH was prepared and used to catalyze glucose transform into HMF. The γ-AlOOH owned the high catalytic activity and the well 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 of DMSO. More importantly, the catalyst γ-AlOOH could be reused for several times without the loss of its significant catalytic activities. After five reaction runs, a HMF with 57.23 % yield and 59.25 % selectivity was obtained. Furthermore, the degradation of other polysaccharides (Maltose, Sucrose and Cellulose) catalyzed by the γ-AlOOH were also investigated under the mixed systems of ionic liquid 1-butyl-3-methylimidazolium chloride, DMSO and a small amount of water. For instance, a high HMF yield of 50.26 % was obtained at 170 °C for 2.5 h on the decomposition of Cellulose.

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References

1. Goldemberg J. Ethanol for a sustainable energy future. *Science* **2007**, *31*, 808-810
2. Caes B. R.; Teixeira R. E.; Knapp K. G.; Raines R. T. Biomass to Furanics: Renewable Routes to Chemicals and Fuels. *ACS Sustainable Chem. Eng.* 2015, *3*, 2591- 2605
3. DaVià L.; Gonzalez-Yañez C.R. E.O.; Davies T.E.; Lopez-Sanchez J.A. Visible light selective photocatalytic conversion of glucose by TiO_2. A*ppl.Catal. B-Environ.* 2017, *202*, 281-288
4. Eblagon K. M.; Pereira M.F.R.; Figueiredo J. L. One-pot oxidation of cellobiose to gluconic acid Unprecedented high selectivity on bifunctional gold catalysts over mesoporous carbon by integrated texture and surface chemistry optimization. A*ppl.Catal. B-Environ.* **2016**,184, 381-396
5. Shamsul N.S.; Kamarudin S.K.; Rahman N.A. Study on the physical and chemical composition of agro wastes for the production of 5-hydroxymethylfurfural. *Bioresour. Technol*. **2018**,*247*, 821-828
6. Mukherjee A.; Dumont M.; Raghavan V. Review: Sustainable production of hydroxymethylfurfural and levulinic acid: Challenges and opportunities. *Biomass Bioenerg.* **2015**, *72*, 143-183
7. Zhang Z. H.; Deng K. Recent Advances in the Catalytic Synthesis of 2,5-Furan- dicarboxylic Acid and Its Derivatives. *ACS Catal.* **2015**, *5*, 6529 -6544
8. Siankevich S.; Fei Z.; Yan N.; Dyson P.J. Application of Ionic Liquids in the Downstream Processing of Lignocellulosic Biomass. *CHIMIA International Journal for Chemistry* **2015**, *69*, 592-596
9. Rosatella A. A.; Simeonov S. P; Frade R.F.M.; Afonso C.A.M. ChemInform Abstract: 5-Hydroxymethylfurfural (HMF) as a Building Block Platform: Biological Properties, Synthesis and Synthetic Applications. *Green Chem.* **2011**, *13*, 754-793
10. Zakrzewska M. E.; Bogel-Łukasik E.; Bogel-Łukasik R. Ionic Liquid-Mediated Formation of 5-HydroxymethylfurfuralsA Promising Biomass-Derived Building Block. *Chem. Rev.* **2011**,111, 397-417
11. Yang Y.; Hu C.W.; Abu-Omar M. M. Conversion of glucose into furans in the presence of $AlCl_3$ in an ethanol-water solvent system. *Bioresour. Technol.* **2012**, 116, 190-194
12. Matsumiya H.; Hara T. Conversion of glucose into 5-hydroxymethyl- furfural with boric acid in moltenmixtures of choline salts and carboxylic acids. *Biomass Bioenerg.* **2015**, 72, 227-232
13. Tong X.; Li M.; Yan N.; Ma Y.; Dyson P. J.; Li Y. Defunctionalization of fructose and sucrose: Iron-catalyzed production of 5-hydroxymethylfurfural from fructose and sucrose. *Catal. Today* **2011**, *175*, 524-527
14. Jain A.; Shore A.M.; Jonnalagadda S.C.; Ramanujachary K.V.; Mugweru A. Conversion of fructose, glucose and sucrose to 5-hydroxymethyl-2-furfural over mesoporous zirconium phosphate catalyst. *Appl. Catal. A* **2015**, *489*,72-76
15. Zhang X.; Wilson K.; Lee A.F. Heterogeneously catalyzed hydrothermal processing of C5-C6 sugars, *Chem. Rev.* **2016**,*116*, 12328-12368
16. Dhepe P.L.; Fukuoka A. Cellulose conversion under heterogeneous catalysis. *ChemSusChem* **2008**,*1*, 969–975.
17. Dijkmans J.; Gabriels D.; Dusselier M.; de Clippel F.; Vanelderen P.; Houthoofd K.; Malfliet A.; Pontikes Y.; Sels B. F. Productive sugar isomerization with highly active Sn in dealuminated β zeolites . *Green Chem.* **2013**, *15*,2777-2785

18. Li H.; Fang Z.; Luo J.; Yang S. Direct conversion of biomass components to the biofuel methyllevulinate catalyzed by acid-base bifunctional zirconia-zeolites. *Appl.Catal. B-Environ.* **2017** , *200*, 182-191
19. Catrinck M. N.; Ribeiro E. S.; Monteiro R.S.; Ribas R. M.; Barbosa M.H.P.; Teófilo R. F. Direct conversion of glucose to 5-hydroxymethylfurfural using a mixture of niobic acid and niobium phosphate as a solid acid catalyst. *Fuel* **2017**, *210*, 67-74
20. Hu L.; Zhao G.; Tang X.; Wu Z.; Xu J.X.; Lin L.; Liu S. J. Catalytic conversion of carbohydrates into 5-hydroxymethylfurfural over cellulose-derived carbonaceous catalyst in ionic liquid. *Bioresour. Technol.* **2013**,*148*, 501-507
21. Sun Z.; Wang S. T.; Wang X. H.; Jiang Z. J. Lysine functional heteropolyacid nanospheres as bifunctional acid-base catalysts for cascade conversion of glucose to levulinic acid. *Fuel* **2016**, *164*, 262-266
22. Chen D. W.; Liang F. B.; Feng D. X.; Xian M.; Zhang H. B.; Liu H. Z.; Du F. L. An efficient route from reproducible glucose to 5-hydroxymethylfurfuralcatalyzed by porous coordination polymer heterogeneous catalysts. *Chem. Eng. J.* **2016,** *300*, 177-184
23. Lopes M.; Dussan K.; Leahy J. J.; DaSilva V. T. Conversion of d-glucose to 5-hydroxymethylfurfural using Al_2O_3-promoted sulphated tin oxide as catalyst. *Catal. Today* **2017,** *279*, 233-243
24. Liu J.; Li H.; Liu Y.; Lu Y. M.; He J.; Liu X. F.; Wu Z. B.; Yang S. Catalytic conversion of glucose to 5-hydroxymethylfurfural over nano-sized mesoporous Al_2O_3-B_2O_3 solid acids. *Catal. Commun.* **2015,** *62*, 19-23
25. Graça I.; Iruretagoyena D.; Chadwick D. Glucose isomerisation into fructose over magnesium-impregnated NaY zeolite catalysts. A*ppl.Catal. B-Environ.* **2017** ,*206*, 434-443
26. Delidovich I.; Palkovits R. Fructose production via extraction-assisted isomerization of glucose catalyzed by phosphate. *Green Chem.* **2016,** 18, 5822-5830
27. Li F.; Shi G. F.; Wang G. Y.; Guo T. C.; Lei X. M. Catalytic conversion of raw Dioscorea composita biomass to 5-hydroxymethylfurfural using a combination of metal chlorides in N, N-dimethylacetamide solvent containing lithium chloride. *Res. Chem. Intermed.* **2016,** 42, 6757-6767
28. Xia H.; Hu H.; Xu S.; Xiao K.; Zuo S. Catalytic conversion of glucose to 5-hydroxymethyfural over Fe/β zeolites with extra-framework isolated Fe species in a biphasic reaction system. *Biomass Bioenerg.* **2018**,*108*, 426–432
29. Hou Q. D.; Zhen M.N.; Liu L.; Chen Y.; Huang F.; Zhang S.Q.; Li W. Z.; Ju M.T. Tin phosphate as a heterogeneous catalyst for efficient dehydration of glucose into 5-hydroxymethylfurfural in ionic liquid. *Appl.Catal. B-Environ.* **2018,** *224*,183-193
30. Jiang L.; Zhou L.; Chao J.; Zhao H.; Lu T.; Su Y.; Yang X.; Xu J. Direct catalytic conversion of carbohydrates to methyl levulinate: Synergy of solid Brønsted acid and Lewis acid. A*ppl.Catal. B-Environ.* **2018,** *220* , 589–596
31. Wei W.; Wu S. Depolymerization of cellulose into high-value chemicals by using synergy of zinc chloride hydrate and sulfate ion promoted titania catalyst. *Bioresour. Technol.* **2017**, *241*,760–766
32. Li Y.N.; Wang J. Q.; He L. N.; Yang Z. Z.; Liu A. H.; Yu B.; Luan C.R. Experimental and theoretical studies on imidazolium ionic liquid-promoted conversion of fructose to 5-hydroxymethylfurfural. *Green Chem.* **2012,***14*, 2752-2758
33. Gomesa F.N.D.C.; Mendesb F.M.T.; Souza M.M.V.M. Synthesis of 5-hydroxymethylfurfural from fructose catalyzed by phosphotungstic acid. *Catal.Today* **2017,** *279*; 296-304
34. Sanchez-Valente J.; Bokhimi X.; Hernandez F. Physicochemical and catalytic properties of sol gel aluminas aged under hydrothermal conditions. *Langmuir* **2003**, *19(9*), 3583 - 3588
35. Chiche D.; Digne M.; Revel R.; et al. Accurate determination of oxide nanoparticle size and shape based on X-Ray powder pattern simulation: application to boehmite AlOOH. *J. Phys. Chem. C* **2008**, *112 (23*,8524-8533
36. Tang Z.; Liu Y. Q.; Li G.C.; Hu X. F.; Liu C. G. Ionic liquid assisted hydrothermal fabrication of hierarchically organized γ-AlOOH hollow sphere. *Materials Research Bulletin.* **2012**, *47(11)*, 3177-3184
37. Wang Y. G.; Bronsveld P. M.; DeHosson J. T. M. Ordering of octahedral vacancies in transition aluminas. *J. Am. Ceram. Soc.* **1998**; *81 (6)*, 1655-1660

38. Tang Z.; Hu X. F.; Liang J. L.; Zhao J. C.; Liu Y. Q.; Liu C. G. Manipulating the morphology and textural property of γ-AlOOH by modulating the alkyl chain length of cation in ionic liquid. *Materials Research Bulletin*. **2013,** *48(6)*, 2351-2360
39. Takagaki A.; Jung J.C.; Hayashi S. Solid Lewis acidity of boehmite g-AlO(OH) and its catalytic activity for transformation of sugars in water. *RSC Adv*. **2014,** *4*, 43785-43791
40. Li G.C.; Liu Y. Q. ; Tang Z. ; Liu C.G. Effects of rehydration of alumina on its structural properties, surface acidity; and HDN activity of quinolone. *Appl. Catal. A* **2012,** *437–438*, 79-89
41. Emeis C. A. Determination of Integrated Molar Extinction Coefficients for Infrared Absorption Bands of Pyridine Adsorbed on Solid Acid Catalysts. *J. Catal.* **1993**, *141*, 347–354.
42. Saravanan K.; Tyagi B.; Shukl Ram S.; Bajaj H.C. Esterification of palmitic acid with methanol over template-assisted mesoporous sulfated zirconia solid acid catalyst. d. A*ppl.Catal. B-Environ*. **2015,** *172–173*, 108-115
43. Hu Z., Liu B.; Zhang Z.; Chen L.. Conversion of carbohydrates into 5-hydroxymethylfurfural catalyzedby acidic ionic liquids in dimethyl sulfoxide. *Industrial Crops and Products* **2013,** *50* , 264– 269
44. Holm J.; Lassi U.; Hernoux-Villie`re A. Task-specific ionic liquid [SBMIM]Cl in one-step dissolution and hydrolysis of fibre sludge. *Biomass Bioenerg.* **2013,** *56*, 432-436
45. Wiredu B.; Amarasekara A. S. Synthesis of a sulfonic acid functionalized acidic ionic liquid modified silica catalyst and applications in the hydrolysis of cellulose. *Catal. Commun.* **2014,***48*,41–44
46. Amarasekara A. S.; Williams L. D.; Ebede C.C. Mechanism of the dehydration of D-fructose to 5-hydroxymethylfurfural in dimethyl sulfoxide at 150 degrees C: an NMR study. *Carbohydr. Res.* **2008,** *343*, 3021-3024
47. Tsilomelekis G.; Josephson T.R.; Nikolakis V.; Caratzoulas S. Origin of 5-hydroxymethylfurfural stability in water/dimethyl sulfoxide mixtures.*ChemSusChem* **2014**, *7*, 117-126
48. Morales G.; Paniagua M.; Melero J.A.; Iglesias J. Efficient production of 5-ethoxymethylfurfural from fructose by sulfonic mesostructured silica using DMSO as co-solvent. *Catal. Today* **2017**,*279*, 305-316
49. Lane D. R.; Masca M.; Stroeve P. Experimental studies towards optimization of the production of 5-(chloromethyl)furfural (CMF) from glucose in a two-phase reactor. *Renew Energ.* **2016,** *85*, 994-1001
50. Zhang L.X.; Xi G.Y.; Chen Z.; Qi Z.Y.; Wang X. C. Enhanced formation of 5-HMF from glucose using a highly selective and stable SAPO-34 catalyst. *Chem. Eng. J.* **2017**, *307*, 877-883
51. Paul S. K.; Chakraborty St. Microwave-assisted ionic liquid-mediated rapid catalytic conversion of non-edible lignocellulosic Sunn hemp fibres to biofuels. *Bioresource Technology* **2018,** *253* , 85–93
52. Siankevich S.; Fei Z.; Scopelliti R.; Laurenczy G.; Katsyuba S.; Yan N.; Dyson P. J.. Enhanced Conversion of Carbohydrates to the Platform Chemical 5-Hydroxymethylfurfural Using Designer Ionic Liquids. *ChemSusChem* **2014,** *7(6)*, 1647-1654
53. Zhou J.; Tang Z.; Jiang X.; Jiang R.; Shao J.; Han F.; Xu Q. Catalytic Conversion of Glucose into 5-Hydroxymethyl-Furfural Over Chromium-Exchanged Bentonite in Ionic Liquid-Dimethy Sulfoxide Mixtures. *Waste Biomass Valor.* **2016**, *7*, 1357–1368
54. Kaijun Dong; Jun Zhang; Weimin Luo; Lin Su Zhilin Huang. Catalytic conversion of carbohydrates into 5-hydroxymethyl furfural over sulfonated hyper-cross-linked polymer in DMSO. *Chem. Eng. J.* **2018**,*334* , 1055–1064
55. Dou Y; Zhou S; Oldani C; Fang W; Cao Q. 5-Hydroxymethylfurfural production from dehydration of fructose catalyzed by Aquivion@silica solid acid. *Fuel* **2018,***214* , 45–54
56. Morales G.; Paniagua M.; Melero J.A.; Iglesias J. Efficient production of 5-ethoxymethylfurfural from fructose by sulfonic mesostructured silica using DMSO as co-solvent. *Catal. Today* **2017**,279, 305 -316