Contents lists available at ScienceDirect





Carbohydrate Research

journal homepage: www.elsevier.com/locate/carres

Direct conversion of cellulose to 5-hydroxymethylfurfural (HMF) using an efficient and inexpensive boehmite catalyst



Zhe Tang, Jianhui Su

School of Chemistry & Chemical Engineering, Yancheng Institute of Technology, Yancheng, Jiangsu Province, 224051, PR China

ARTICLE INFO ABSTRACT Keywords: High efficiency conversion of cellulose to 5-hydroxymethylfurfural (HMF) remains a challenge today. A simple Cellulose solid acid catalyst Boehmite (y-AlOOH) with high hydrothermal stability was prepared and used as sole catalyst HMF for the direct conversion of cellulose into HMF in mixed reaction solvents of ionic liquid 1-buthyl-3-methyli-Boehmite midazolium chloride (BmimCl) and dimethyl sulfoxide (DMSO). This was aimed at developing an efficient and Heterogeneous catalysis inexpensive catalyst for the production of HMF. The effects of factors such as water, solvent, catalyst load, Carbohvdrates temperature and reaction duration were investigated. An impressive HMF yield of 58.4% with 97.2% cellulose conversion was obtained at 160 °C after 2 h. More importantly, the catalyst γ -AlOOH was reused several times without loss of its catalytic properties. After five reaction runs, an HMF yield of 47.8% with 91.0% conversion was also obtained. In addition, the catalyst Y-AlOOH displayed excellent catalytic effects on the degradation of

1. Introduction

Factors such as diminishing petroleum sources and growth in demand for energy and chemicals have aroused extensive interest in the attainment of sustainability in conversion of abundant and renewable biomass into platform chemicals [1,2]. Studies have identified 5-hydroxymethylfurfural (HMF) as an important biomass platform chemical since it is widely used as a versatile building block for synthesis of fine chemicals, medicines, bio-fuels and monomers of polymers [3,4]. Therefore, the synthesis of 5-HMF from carbohydrates has attracted a lot of attention. Generally, excellent yields of HMF can be obtained using simple monosaccharides like fructose and glucose as reactants under various catalytic systems. However, apart from serving as resources in food industries, monosaccharides are expensive and not readily available [5]. In contrast, cellulose is an abundant, less expensive and non-edible carbohydrate, and a more promising material for use in the production of HMF [6]. However, the robust structure of cellulose and instability of HMF under harsh reaction conditions create some problems in the degradation of cellulose to HMF, often resulting in poor yield of HMF [7-9].

Decades of research have demonstrated that acid catalysts accelerate the degradation of cellulose [10–12]. This process consists of two categories: homogeneous acid catalysis and heterogeneous acid catalysts. Studies have shown that homogeneous acid catalysts are efficient in the degradation of cellulose to HMF. These catalysts are mineral acids [13], heteropolyacids [14], ionic liquids [15], and metal chlorides [16-18]. However, the use of homogenous acid catalysts gives rise to serious problems related to corrosion of equipment, separation of catalysts from products, and waste treatment [19]. On the other hand, heterogeneous acid catalysts have numerous advantages such as easy separation and recycling, low cost, and low environmental hazards [20,21]. Therefore, various heterogeneous catalysts such as metal oxides [22], zeolites [23], sulfonated carbon-based materials [24], polymers [25], fused salts [26], metal-organic frameworks [27] and resins [28] have been developed and used to degrade cellulose or saccharides into HMF. Among these heterogeneous catalysts, metal oxides are the most commonly used due to their property-tunable solid acids [29]. Aluminum oxide (Al_2O_3) has been reported to possess high activity in the production of HMF [30-34]. For instance, Sampath [30] investigated the effect of Al₂O₃ on the conversion of glucose to HMF. A High HMF yield of 56% was obtained in DMSO system at 130 °C after 3 h in the presence of some amount of copper chloride (CuCl₂, 0.6 mmol). It has been discovered that the reaction system could also convert disaccharides and starch into HMF. Garcia-Sancho [32] found that Al₂O₃, when used as support for Nb₂O₅, enhanced the dehydration of xylose. However, the hydrothermal stability of Al₂O₃ is low. Thus, it

other carbohydrates. High yields of HMF from other carbohydrates such as glucose (61.2%), starch (62.7%) and inulin (70.5%) were achieved using γ -AlOOH as the catalyst. The proposed catalytic method shows a promising potential for HMF preparation, especially for industrial-scale HMF production from renewable bioresources.

E-mail address: sujianhui999_888@163.com (J. Su).

https://doi.org/10.1016/j.carres.2019.06.010

Received 18 March 2019; Received in revised form 9 June 2019; Accepted 17 June 2019 Available online 21 June 2019

0008-6215/ © 2019 Published by Elsevier Ltd.

^{*} Corresponding author.

is easily converted to its precursor boehmite (γ -AlOOH) at temperatures above 150 °C in hot water systems [35]. This is not beneficial for the degradation of cellulose since the conversion of cellulose often requires addition of some water to accelerate the hydrolytic reaction at temperatures usually higher than 150 °C.

Boehmite (γ -AlOOH) is one of the Al₂O₃ precursors with high hydrothermal stability; it is easy to prepare, and it is cheap [36,37]. Studies by Takagaki et al. [38] revealed that γ -AlOOH can catalyze the conversion of glucose to HMF in water systems. This finding inspired the idea that γ -AlOOH may be an efficient catalyst in the conversion of cellulose or other carbohydrates to HMF. To the best of our knowledge, there are few reports on conversion of cellulose or other carbohydrates to HMF using γ -AlOOH as catalyst.

The degradation of cellulose to HMF is a tandem reaction involving hydrolysis of cellulose into glucose, isomerization of glucose to fructose, and dehydration of fructose to HMF [39]. Hence, the first reaction step (the hydrolysis) is very important. However, due to the robust structure of cellulose, cellulose is sparingly soluble in water and most organic solvents [7–9]. Hence, the choice of a suitable solvent is also crucial in the production of HMF from cellulose. Research has demonstrated that ionic liquid (IL) is a promising solvent for dissolution of cellulose due to the strong interaction between its anion and hydroxyl of cellulose [40–42]. Although IL is more expensive than common solvents, it can be recycled many times or mixed with other solvents e.g. DMSO so as to reduce its cost, since it has high thermal and chemical stability and low vapor pressure [43].

In the present study, γ -AlOOH was first employed to degrade cellulose into HMF using IL (1-butyl-3-methylimidazolium chloride, BmimCl) and DMSO as the reaction solvents. Reaction conditions such as reaction duration, reaction temperature, catalytic loading, water content and reaction solvents were carefully investigated. This was with the aim of establishing optimum reaction parameters for high catalytic efficiency in the conversion of cellulose to HMF, and understanding the possible reaction mechanism(s). Furthermore, the catalyst was characterized using many technologies such as XRD, FT-IR, Py-IR, TEM, BET and TG.

2. Experimental

2.1. Materials

The ionic liquid (IL) 1-buthyl-3-methylimidazolium chloride (BMIMCl, AR) was purchased from Shanghai Cheng Jie Chemical Co. Ltd. (Shanghai, China), while HMF standard sample (AR) was acquired from Aladdin Reagent Co. Ltd. (Shanghai, China). Microcrystalline cellulose (MCC) (average particle size $50 \,\mu$ m) was supplied by Sinopharm Chemical Reagent Co. Ltd. (Beijing, China). All other reagents were analytically pure pharmaceuticals from Sinopharm Chemical Reagent Co. Ltd, and were used without purification.

2.2. Preparation of catalyst

The catalyst (γ -AlOOH) was prepared via hydrothermal synthesis. The procedure for preparing the γ -AlOOH was as follows: 40 mL of 0.75 M NH₄HCO₃ was slowly added to 10 mL of 1.5 M Al(NO₃)₃·9H₂O, with magnetic stirring at 800 rpm. Then, 25% ammonia water was added to the clear solution until the pH reached 9. Thereafter, the solution was transferred into a 100-mL Teflon-lined stainless autoclave, sealed, and then heated at 150 °C for 12 h. After the autoclave was naturally cooled to room temperature, the resultant solid was collected through centrifugation and washed three times with deionized water. Finally, the catalyst (γ -AlOOH) was obtained through vacuum-drying at 80 °C for 24 h.

2.3. Catalyst characterization

Powder XRD patterns were determined using Panalytical X-ray Powder diffractometer (XRD) with Cu-K α radiation ($\lambda = 1.5406$ Å). The data were recorded at a 2θ range of 5° to 80°. Fourier transform infrared (FT-IR) analysis was done with Nexus Nicolet Fourier Transform spectrometer (Madison, Wisconsin, USA) in the range of wavelengths of $4000-500 \text{ cm}^{-1}$. Specific surface area and pore size were determined using Quantachrome Micromeritics Instrument with ASAP 2020 system (Norcross, GA, USA), Brunauer-Emmett-Teller (BET) equation and Barrett-Joyner-Halenda (BJH) method, as appropriate. Morphology and microstructure were assessed through transmission electron microscopy (TEM, JEM-2100UHR; JEOL Ltd., Tokyo, Japan). Thermal gravimetric analyses (TGA) of the samples were performed on TA thermal gravimetric analyzer at a heating rate of 10 °C/min under air-atmosphere (SDT Q600, Newcastle, Delaware, USA). Lewis and Brønsted acidic sites were investigated via FT-IR pyridine adsorption technique (Py-FTIR; Nicolet, Madison, Wisconsin, USA). 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 measurements, the samples were degassed in air at 150 °C for 5 h, cooled down, and then adsorbed in saturated pyridine atmosphere at room temperature for 5 h. After adsorption, the infrared spectrum was recorded with sample temperature fixed at 150 °C while outgassing. The number of Lewis acid sites was determined on the basis of the integral absorbance of the characteristic band at 1450 cm⁻¹, using integrated molar extinction coefficient 2.22 cm mmol⁻¹ [44,45].

2.4. Typical procedure in the production of HMF from cellulose

The experiments were carried out in an $18 \text{ mm} \times 180 \text{ mm}$ glass tube with a lid. In a typical reaction process, 100 mg microcrystalline cellulose (MCC) was added to a mixed solution consisting of 4.0 g IL (BmimCl) and 2.0 g DMSO under magnetic stirring. When MCC was dissolved in the IL-containing solvents, 100 mg of the catalyst (y-AlOOH) and 1.0 mL deionized water were added to the reaction. The resultant solution was heated to 160 °C and reaction was allowed for 2.0 h, with magnetic stirring at 800 rpm. The reaction mixture was quickly cooled to room temperature through addition of 20 mL cold deionized water. After centrifugation at 10000 rpm for 5 min, the clear solution and solid were separated, and the solid was weighed. The clear solution was used to analyze the distribution and contents of the reaction products. The solid was washed several times in deionized water and ethanol, dried and weighed. This first weight of solid was designated W1. Then, the solid was further washed thrice using y-valerolactone, dried and weighed. This second weight of the solid was tagged W₂. The dried solid was used as spent catalyst for the next reaction on recyclable experiments of the catalysts. The difference in the weight between W1 and W2 was the mass of residual cellulose, based on the fact that y-valerolactone can dissolve cellulose, while water and ethanol cannot dissolve cellulose [46]. Hence the conversion of cellulose was calculated according to the following equation:

Cellulose conversion(%) = 100 % - $\frac{Mass of residual cellulose}{Mass of starting cellulose} \times 100\%$

2.5. HPLC analysis

Following filtration through a 0.22 μ m filter, the collected clear liquids were analyzed using High Performance Liquid Chromatography (HPLC, Agilent 1200, USA). The concentrations of HMF were quantified with HPLC equipped with an ultraviolet detector (UV-9600, Beijing, China) at ultraviolet wavelength of 284 nm. The eluent was a mixture of methanol and water at a volumetric ratio of 2:8, and the flow rate was 0.6 mL min⁻¹. The concentrations of glucose, fructose, levulinic acid

(LA) and formic acid (FA) were also determined using the same HPLC outfitted with a refractive index (Agilent G1362A) and an Bio-Rad ion-exclusion column (300 mm \times 7.8 mm, Aminex HPX-87H, Beijing, China) at 60 °C. The mobile phase was 0.004 M H₂SO₄ at a flow rate of 0.45 mL min⁻¹. The yields of HMF and glucose were calculated according to the following equations:

Glucose yield (%)

 $= \frac{Moles of glucose in product}{Moles of cellulose load in the reaction (base on glucose unit)} \times 100\%$

HMF yield (%)

= <u>Moles of HMF in product</u> <u>Moles of cellulose load in the reaction (base on glucose unit)</u> × 100%

3. Results and discussion

3.1. Characterization of the catalyst

The XRD pattern of the catalyst (γ -AlOOH) is depicted in Fig. S1. All the diffraction peaks were due to the characteristic peaks of an orthorhombic γ -AlOOH (JCPDS Card 021–1307). No other peaks were observed, which indicated that γ -AlOOH was successfully synthesized. The FT-IR spectroscopy was carried out in order to confirm the formation of γ -AlOOH (shown in Fig. S2). All bands of characteristic groups in γ -AlOOH were in Fig. S2. The bands at 3310, 3090, 1072 and 1162 cm⁻¹ were assigned to the characteristic vibrations of ν_{as} (Al)O–H, ν_{s} (Al)O–H, δ_{s} Al–O–H and δ_{as} Al–O–H, respectively, while the bands at 751, 630, and 484 cm⁻¹ belonged to the vibration mode of AlO₆.

The N₂ absorption and desorption isotherm of γ -AlOOH is depicted in Fig. 1. It can be seen that the isotherm was a type IV isotherm with a type H₂ hysteresis loop above 0.4 P/P0, indicating the existence of meso-pores and relatively uniform distribution of pore size. The pore size distribution is also shown in Fig. 1 (the inset image). Most pores were of size 2.9 nm. Only a few pores were up to 10.2 nm. The other textural properties of γ -AlOOH can be seen Table 1. In order to investigate the morphology and surface structure of the γ -AlOOH, TEM was carried out, and its image is displayed in Fig. S3. It was discovered that γ -AlOOH consisted of a great number of irregular nanosheets with mean length of about 200 nm and the surfaces of the nanosheets were not smooth. There were a vast number of small pores, which might explain the observation that most of pores were 2.9 nm in size.



Fig. 1. N_2 adsorption and desorption isotherms and Pore size distribution (inset) of the $\gamma\text{-AlOOH}.$

Thermogravimetric analysis of γ -AlOOH was also carried out. As shown in Fig. S4, three stages of weight loss were observed. Stage 1 was at temperature range of 30–190 °C, which was attributable to the volatilization of the adsorbed waters on the surfaces of γ -AlOOH [47]. However, the weight loss was slight (less than 2.0%). Stage 2 wt loss occurred at temperature range of 190–710 °C, and accounted for most of the weight loss (up to 41.0%). This weight loss was due to transformation as a result of dehydration of γ -AlOOH to γ -Al₂O₃ [48]. Stage 3 wt loss occurred above 710 °C, and was due to crystal transformation from γ -Al₂O₃ to α -Al₂O₃ [49]. The stage-3 weight loss was also very slight and negligible (less than 0.5%). These results indicate that at reaction temperatures was below 190 °C, γ -AlOOH was stabilized and did not change to other phases or decompose.

Fig. 2 shows results of Py-FTIR for γ -AlOOH. Only the absorption peaks of Lewis acid sites appeared, which were at 1592 cm⁻¹, 1486 cm⁻¹, and 1450 cm⁻¹. There were no pyridine absorption peaks of Brønsted acid sites (at 1540 cm⁻¹) [35]. The results demonstrate that γ -AlOOH acted as a Lewis acid catalyst without the Brønsted acid sites. The amount of acid and acid site density per site of γ -AlOOH were about 83 µmol g⁻¹ and 0.2 per nm², respectively, using integrated molar extinction [44,45].

3.2. Results of degradation of cellulose into HMF

Table 2 shows the results of comparison of catalytic effectiveness between γ -AlOOH and current best-acting catalysts as regards conversion of cellulose to HMF. The results indicated that y-AlOOH (entry 14-16) exhibited excellent catalytic effects in the degradation of cellulose to HMF. In the absence of the catalyst γ -AlOOH, HMF yield (entry 16) was only 11.3%, with low cellulose conversion of 55.7%. However, after adding the catalyst, a higher HMF yield of 58.4% was achieved with high cellulose conversion (97.2%). The performance of γ -AlOOH was similar to that of the homogenous catalytic systems of IL and metal chlorides (Entry 3,4) and bi-phase catalytic systems with metal chlorides (entry 2), but higher than those of the catalytic systems using IL as the only catalysts (entry 5,6), and normal heterogeneous catalysts (entry 9, 10, 13). Furthermore, it was lower than that of novel catalytic systems, including mixture of novel strong acid IL and metal chlorides (entry 7), novel hybrid solid polymer (entry 8), novel metal-doped carbon materials (entry 11) and a new material (entry 12). The results suggest that the catalytic effect of y-AlOOH was similar to those of metal chlorides. In previous studies [17,44,45], the catalytic mechanism involved in the metal chloride-catalyzed conversion of cellulose to HMF was shown to entail acceleration of the hydrolysis of cellulose to glucose with acid generated from their hydration, promotion of isomerization of glucose to fructose and dehydration of fructose to HMF, due to their Lewis acidity. The catalyst γ-AlOOH is a typical Lewis acid catalyst. Therefore, the possible catalytic mechanism of y-AlOOH involves Lewis acid-induced enhancement of glucose isomerization to fructose, and fructose dehydration into HMF. Furthermore, the surface hydroxyl groups of y-AlOOH might produce weak acidity and accelerate the hydrolysis of cellulose into glucose with assistance of IL. However, the use of homogenous metal salts (metal chlorides) lead to serious problems such as equipment corrosion and waste treatment. Studies have shown that y-AlOOH is a readily available, low-cost heterogeneous catalyst which is easily separated from products, and is suitable for large-scale production of HMF, unlike the novel catalysts ((entries 7, 8, 11 and 12) which are either complex to prepare or expensive.

3.3. Optimization of reaction parameters

3.3.1. Reaction temperature and time

In order to obtain optimized HMF yield, the degradation of cellulose to HMF was monitored as a function of time at different temperatures. Since the hydrolysis, isomerization and dehydration reactions in the three-step tandem for conversion of cellulose to HMF are endothermic

Table 1

Textural	and	acid	properties	of γ-AlOOH.	

BET surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore size (nm)	Amount of acid ^a (umol g^{-1})	Density of acid sites (sites per nm ²)
316	0.2	3.1	83	0.2
^a Pyridine-IR				



Fig. 2. Py-FTIR spectrum of the γ-AlOOH.

[58,59], elevated temperature was beneficial for the generation of HMF, as shown in Fig. 3. A maximum HMF yield and selectivity (58.4%, 60.1%) were obtained at 160 °C for 2 h. Further elevation of reaction temperature to 170 °C and 200 °C led to decomposition and condensation of HMF into other compounds after 2 h reaction time. The HMF yield and selectivity were decreased correspondingly. Furthermore, as depicted in Fig. 3, prolongation of the reaction over optimized time was not beneficial for the production of HMF, indicating that longer reaction time would lead to side-reactions. Hence, the optimal temperature

Table 2

Overview of HMF	Yields from the	degradation of	Cellulose in the	Best-Behaving	Catalytic System.
		0			2 2

and time were 160 °C and 2 h, respectively. These were used in subsequent discussion of other reaction parameters.

3.3.2. Catalyst loading

With regard to the loading of the catalyst γ -AlOOH as shown in Fig. 4, cellulose conversion and HMF yield were increased at increased doses of catalyst. When the amount of γ -AlOOH was 0.1 g, the yield of HMF was 58.4%, and cellulose conversion was 97.2%. Further increases in dose of γ -AlOOH led to decrease in HMF yield and selectivity, as well as increases in side reaction products (LA and FA). These suggest that excess catalyst would lead to decomposition of HMF into side products. Hence, the optimal dose of γ -AlOOH was 0.1 g, which was used for subsequent experiments.

3.3.3. Reaction solvents

From Table 2, it can be seen that in the absence of DMSO (entry 14), an HMF yield of 51.3% was achieved with IL (BMIMCl) in the presence of γ -AlOOH, which meant that the reaction solvent had a great effect on the degradation of cellulose. As shown in Fig. 5, among the single solvents, IL produced the best catalytic performance in which the HMF yield and selectivity were 51.3% and 54.1%, respectively. With other solvents (DMSO, acetone, THF and DMF), the HMF yields were very little (not more than 3.0%), which might be attributed to the robust structure of cellulose, which is sparingly soluble in water and in most common organic solvents [7–9]. However, cellulose was easily dissolved in IL due to the strong interaction between the IL anion and hydroxyl groups of cellulose [40–42]. However, in view of high cost and high viscosity of IL, some common solvents were introduced in the system. Studies have shown that an aprotic solvent could maintain the

Entry	Substrate	Solvent	Catalyst	T ^a (°C)	Time	C ^b (%)	Y ^c (%)	Ref.
1	Cellulose (40 mg)	THF(3 mL)-H ₂ O (1 mL)- NaCl	AlCl ₃ ·6H ₂ O (0.1 mmol)	180 (microwave)	0.5 h	99.0	37.0	16
2	Cellulose (50 mg)	THF(6 mL)-H ₂ O (1 ml)	NaCl (30 wt%)	200	6 h, 8 h	> 99	56.1,58.9	17
3	Cellulose	BmimCl (1 g)	CrCl ₃ ·6H ₂ O (15mg0	150 (microwave)	10 min	> 99	54.0	49
	(50 mg)							
4	Cellulose (50 mg)	EmimCl (0.5 g)	$CuCl_2/CrCl_2$ (37µmol/g, $X_{CuCl_2} = 0.17$)	120	8 h	> 99	57.5	50
5	Cellulose (0.2 g)	H ₂ O (4 mL)	Cr((DS)H ₂ PW ₁₂ O ₄₀) ₃ (0.06 mmol)	150	2 h	77.1	52.7	14
6	Cellulose (0.1 g)	BmimCl (2.0 g)	Cr((PSMIM)HSO ₄) ₃ (0.05 g)	120	5 h	95.0	53	51
7	Cellulose (0.35 g)	$EmimAc(10 mL) + H_2O (0.2 mL)$	$((C_4SO_3Hmim)(CH_3SO_3) (1.5 mL) + CuCl_2$	160	3.5 h	> 99	69.7	15
			(0.1 mol/L)					
8	Cellulose (0.1 g)	MIBK(5 mL)-H2O (0.5 mL)	ChH ₂ PW ₁₂ O ₄₀	140	8 h	87.0	75.0	52
9	Cellulose (0.25)	H ₂ O (10 mL)	Bimodal-HZ-5 (0.50 g)	190	4 h	67.0	46.0	53
10	Cellulose(0.1 g)	THF (6 mL) –H ₂ O (2 mL)-NaCl	Nb-C-50 (0.1 g)	170	8 h	> 99	53.3	54
11	Cellulose (1 g)	H ₂ O (45 mL)	Ni _n /Cs (200 mg)	200	1 h	> 99	85.0	55
		+ H ₂ (6 MPa)						
12	Cellulose (0.1 g)	THF (4 mL) –H ₂ O (1 mL)-NaCl	HfO(PO ₄) _{2.0}	190	4 h	69.8	89.7	56
			(0.03 g)					
13	Cellulose (0.1 g)	BmimCl (2.0 g) $+$ H ₂ O (1.2 mL)	Cr-ACS (0.05 g, $X_{Cr3+} = 5\%$)	120	1 h	> 99	49.0	57
14	Cellulose (0.1 g)	BmimCl (4.0 g) + H_2O (1.0 mL)	γ-AlOOH (0.1 g)	160	2 h	94.8	51.3	This
								work
15	Cellulose (0.1 g)	BmimCl (4.0 g) $+$ DMSO(2.0 g) $+$ H ₂ O	γ-AlOOH (0.1 g)	160	2 h	97.2	58.4	This
		(1.0 mL)						work
16	Cellulose (0.1 g)	BmimCl (4.0 g) + DMSO(2.0 g) + H_2O	Absence	160	2 h	55.7	11.3	This
		(1.0 mL)						work

^a reaction temperature.

^b conversion of cellulose.

^c yield of HMF.



Fig. 3. Effects of reaction time under different temperatures on the HMF yield (a), cellulose conversion (b) and HMF selectivity. Reaction condition: 0.1 g cellulose; 0.1 g γ-AlOOH; 2.0 g DMSO, 4.0 g BMIMCl and 1.0 mL H₂O.



Fig. 4. Effect of catalyst loading on degradation of cellulose. Reaction condition: 0.1 g cellulose; 2.0 g DMSO, 4.0 g BMIMCl and 1.0 mL H_2O ; 160 °C; 2 h.

ability of IL to solubilize cellulose [43]. Moreover, DMSO has the capacity to stabilize HMF and inhibit its decomposition [30,60]. Thus, DMSO was chosen as the added solvent. As showed in Fig. 5, the addition of DMSO had great effect on the degradation of cellulose. When the mass ratio of DMSO was 37.0%, the performance of the reaction solvents (DMSO and IL) was optimum at 58.4%, with cellulose conversion of 97.2%. Further increases in DMSO caused decreases in HMF



Solvents (X₁ is the mass fraction of IL in the mixed solvents of IL and DMSO)

Fig. 5. Effect of solvent on degradation of cellulose. Reaction condition: 0.1 g cellulose; 0.1 g γ -AlOOH; 6.0 g solvent and 1.0 mL H₂O; 160 °C; 2 h.

yield and cellulose conversion. Excessive decrease in IL decreased the solubility of cellulose remarkably and affected the conversion of cellulose to HMF.

3.3.4. Effect of amount of H_2O added

The amount of H_2O added has a great influence on the degradation of cellulose to HMF. Water not only acts as a cross-catalyst or reactant in the hydrolysis of cellulose, it also acts as an inhibitor to the product HMF (by increasing decomposition rate HMF into side-products like LA



Fig. 6. Effect of H_2O on degradation of cellulose. Reaction condition: 0.1 g cellulose; 0.1 g γ -AlOOH; 2.0 g DMSO and 4.0 g BMIMCl; 160 °C; 2 h.



Fig. 7. Distribution of the products. Reaction condition: 0.1 g cellulose; 0.1 g γ -AlOOH; 2.0 g DMSO, 4.0 g BMIMCl and 1.0 mL H₂O; 160 °C.

and FA). Hence, after the addition of H_2O , the rate of hydrolysis of cellulose was increased, and the total reaction rate was promoted correspondingly, causing the amount of all products to increase, as shown in Fig. 6. When the H_2O :cellulose ratio was to 4:1, rate of hydrolysis of cellulose to glucose was maximum, and the highest yield of glucose

(12.4%) was obtained. Correspondingly, further increases in the amount of H_2O led to decreases in the amount of glucose produced, but the amounts of other products were increased. When the H_2O :cellulose ratio was to 10:1, highest yield and selectivity of HMF (58.4% and 60.1%, respectively) were obtained. However, further increases in the amount of H_2O caused increased decomposition of HMF and decreased solubility of cellulose in IL, with corresponding decreases HMF yield and selectivity. Hence, the optimum H_2O :cellulose ratio was 10, and the optimum amount of H_2O was 1.0 g (1.0 mL).

From the above results, it can be concluded that the optimum reaction conditions were 0.1 g cellulose, 0.1 g γ -AlOOH, 2.0 g DMSO, 4.0 g BMIMCl,1.0 mL H₂O, 160 °C, 2 h.

3.4. Distribution of the products

To understand the possible reaction route and distribution of other products, the distribution of the products was investigated at optimum reaction conditions. As depicted in Fig. 7, HMF yield and cellulose conversion increased along with increase in reaction time; highest yield of HMF was 58.4% at 120 min, with cellulose conversion of 97.2%. Further extension of reaction time to 300 min had very little effect on the conversion of glucose. However, HMF yield decreased remarkably to 15.3%, which might be attributed to its decomposition, consistent with variations in the two major side products LA and FA. Glucose and fructose, the predominant intermediates, were detected during the reaction, and achieved high yields of 13.5% and 6.9% at reaction times of 80 min and 100 min, respectively. This indicates that the degradation of cellulose to HMF was a tandem reaction involving hydrolysis of cellulose to glucose, isomerization of glucose to fructose, and dehydration of fructose to HMF.

3.5. Recycling potential of y-AlOOH

The re-usability of γ -AlOOH is not only very important for evaluating the stability of γ -AlOOH, but also necessary for large scale production of HMF from cellulose. Leaching of acid sites and deactivation are the two major problems of the catalyst associated with HMF production. Acid site leaching experiments were carried out via the filtration of γ -AlOOH after running the cellulose degradation for about 60 min at 160 °C, and then the reaction was prolonged for 180 min in the absence of the catalyst γ -AlOOH. As shown in Fig. 8a, HMF yield was not increased, and no further reaction was detected, suggesting that the no acid sites in γ -AlOOH were leached. The stability of γ -AlOOH was also investigated under the reaction conditions indicated in section 2.4. After the reaction, the catalyst γ -AlOOH was recovered via filtration, washed with water, ethanol and γ -valerolactone, and dried



Fig. 8. Time-yield plots of cellulose to HMF conversion, existence γ -AlOOH (solid circle) and removing γ -AlOOH (hollow circle) after 60 min (a) and recycling experiments of the catalyst (b). Reaction condition: 0.1 g cellulose; 0.1 g catalyst; 2.0 g DMSO, 4.0 g BMIMCl and 1.0 mL H₂O; 160 °C; 2 h.

Table 3

Catalytic conversion of various sugars into HMF over the y-AlOOH.

Entry	Sugars	Solvents	Temperature (°C)	Time (h)	Conversion (%)	HMF Yield (%)
1	Cellulose	IL (4.0 g) +DMSO(2.0 g) +H ₂ O (1.0 mL)	160	2	97.2	58.4
2	glucose	DMSO (2.5 g)	130	3	98.6	61.2
3	glucose	IL (2.5 g)	130	3	96.9	41.1
4	glucose	IL + DMSO (2.5 g, IL/DMSO, 2:1 W:W)	130	3	95.3	45.2
5	Starch	IL $(4.0 \text{ g}) + \text{DMSO}(2.0 \text{ g}) + \text{H}_2\text{O} (1.0 \text{ mL})$	160	2	> 99	62.7
6	Inulin	IL (4.0 g) + DMSO(2.0 g) + H_2O (1.0 mL)	160	2	> 99	70.5

Raw materials: 0.1 g cellulose, 0.1 g y-AlOOH.

overnight under vacuum at 100 °C. Then, the spent catalyst was used in the next reaction as a test of its recyclability. As shown in Fig.8b, γ -AlOOH performed well without loss of its catalytic properties. After five reaction runs, an HMF yield of about 47.8% was obtained, with cellulose conversion of 91.0%, which might be attributed to its high hydrothermal stability. The fresh and spent catalysts after five times of reuse were further characterized using XRD and FT-IR. From the patterns of XRD (Fig. S6a) and FT-IR (Fig. S6b), it can be seen that the peaks of the spent γ -AlOOH were almost the same with those of fresh γ -AlOOH. Furthermore, the XRD patterns of the spent γ -AlOOH at different reaction times at 160 °C were also investigated. As shown in Fig. S7, their diffraction peaks were almost the same with those of the fresh γ -AlOOH in Fig. S6a. These results indicate that γ -AlOOH possesses very good hydrothermal stability.

3.6. Conversion of glucose and other carbohydrates to HMF

The catalyst y-AlOOH was tested for its applicability in the conversion of glucose and other carbohydrates. As shown in Table 3, most of the raw materials underwent smooth transformation to their corresponding HMFs, with moderate-to-excellent yields. When glucose was used as raw material, high HMF yield was obtained with DMSO (61.2%), but not with IL (41.1%) or mixture of IL and DMSO (45.2%). This might be attributed to high solubility of glucose in DMSO, good protection of HMF and lower viscosity of DMSO (relative to IL), leading to better catalyst contact with reactants [30,60]. With other carbohydrates like starch and inulin, higher HMF yields were obtained than with cellulose, most likely due to their structural differences. Starch is composed of glucose units linked through α -1, 4 and α -1, 6 glycosidic bonds, whereas cellulose consists of glucose units linked with unbranched β -1,4 glycosidic bonds; it is densely packed due to strong hydrogen bonds [61,62]. Thus, the reactivity of cellulose is inferior to that of starch. Inulin is a polymer of fructose units linked with β -1, 2 glucosidic bonds. It is known that fructose is easier to convert to HMF than glucose [63].

4. Conclusion

A simple solid acid catalyst (γ -AlOOH) was prepared and employed for one-step degradation of cellulose into HMF. The effects of various reaction parameters such as reaction duration, reaction temperature, catalytic loading, amount of added water, and reaction solvents were investigated. The results showed that γ -AlOOH possessed high efficiency and moderate selectivity, and good applicability and stability. A high HMF yield of 58.4% at 97.2% cellulose conversion was obtained at 160 °C at reaction time of 2 h in the mixed solvents of BmimCl and DMSO (6.0 g, 4:2 W/W). Moreover, the catalyst γ -AlOOH was reused several times without loss of its catalytic activities. After five reaction runs, an HMF yield of 47.8% with 91.0% cellulose conversion was also obtained. No acid sites of γ -AlOOH were leached in the reaction. Future studies are ongoing with respect to modification of this catalyst to obtain higher HMF yields and selectivity in water-containing systems, as well as further applications of this catalyst in other fields.

Acknowledgments

This work was supported financially by the Talent Instruction Projects of the Yancheng Institute of Technology (KJC2014015 and XJ201724), the Provincial Education Program of Jiangsu (17KJD530002), and Jiangsu Overseas Visiting Scholar Program for University Prominent Young & middle-aged Teachers and Presidents.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.carres.2019.06.010.

References

- X. Li, R. Xu, J. Yang, S. Nie, D. Liu, Y. Liu, C. Si, Production of 5-hydroxymethylfurfural and levulinic acid from lignocellulosic biomass and catalytic upgradation, Ind. Crops Prod. 130 (2019) 184–197.
- [2] B.R. Caes, R.E. Teixeira, K.G. Knapp, R.T. Raines, Biomass to furanics: renewable routes to chemicals and fuels, ACS Sustain. Chem. Eng. 3 (2015) 2591–2605.
- [3] A.A. Rosatella, S.P. Simeonov, R.F.M. Frade, C.A.M. Afonso, ChemInform abstract: 5-hydroxymethylfurfural (HMF) as a building block platform, biological properties, synthesis and synthetic applications, Green Chem. 13 (2011) 754–793.
- [4] M.E. Zakrzewska, E. Bogel-Łukasik, R. Bogel-Łukasik, Ionic liquid-mediated formation of 5-hydroxymethylfurfurals a promising biomass-derived building block, Chem. Rev. 111 (2011) 397–417.
- [5] A. Mukherjee, M. Dumont, V. Raghavan, Review: sustainable production of hydroxymethylfurfural and levulinic acid, Challenges and opportunities, Biomass Bioenergy 72 (2015) 143–183.
- [6] D. Klemm, B. Heublein, H.P. Fink, A. Bohn, Cellulose:Fascinating biopolymer and sustainable raw material, Angew. Chem. Int. Ed. 44 (22) (2005) 3358–3393.
- [7] F. Yu, R. Zhong, H. Chong, M. Smet, W. Dehaen, B.F. Sels, Fast catalytic conversion of recalcitrant cellulose into alkyl levulinates and levulinic acid in the presence of soluble and recoverable sulfonated hyperbranched poly(arylene oxindole)s, Green Chem. 19 (1) (2017) 153–163.
- [8] S. Kassaye, K.K. Pant, S. Jain, Synergistic effect of ionic liquid and dilute sulphuric acid in the hydrolysis of microcrystalline cellulose, Fuel Process. Technol. 148 (2016) 289–294.
- [9] S. Jing, X. Cao, L. Zhong, X. Peng, R. Sun, J. Liu, Effectively enhancing conversion of cellulose to HMF by combining in-situ carbonic acid from CO₂ and metal oxides, Ind. Crops Prod. 126 (2018) 151–157.
- [10] W.Z. Li, Y.S. Zhu, Y.J. Lu, Q.Y. Liu, S.N. Guan, H.M. Chang, H. Jameel, L.L. Ma, Enhanced furfural production from raw corn stover employing a novel heterogeneous acid catalyst, Bioresour. Technol. 245 (2017) 258–265.
- [11] P.R. Yu, W.C. Hung, H.P. Wan, LiCl/HCl ionic solution for efficient conversion of lignocellulose into glucose under mild conditions, Taiwan. J. Inst. Chem. Eng. 93 (2018) 193–200.
- [12] H. Wang, C. Zhu, D. Li, Q. Liu, J. Tan, C. Wang, C. Cai, L. Ma, Recent advances in catalytic conversion of biomass to 5-hydroxymethylfurfural and 2,5- dimethylfuran, Renew. Sustain. Energy Rev. 103 (2019) 227–247.
- [13] E.E. Harris, B.G. Lang, Hydrolysis of wood cellulose and decomposition of sugar in dilute phosphoric acid, J. Phys. Colloid Chem. 51 (1947) 1430–1441.
- [14] S. Zhao, M. Cheng, J. Li, J. Tian, X. Wang, One pot production of 5-hydroxymethylfurfural with high yield from cellulose by a Brønsted–Lewis–surfactantcombined heteropolyacid catalyst, Chem. Commun. 47 (2011) 2176–2178.
- [15] Z.D. Ding, J.C. Shi, J.J. Xiao, W.X. Gu, C.G. Zheng, H.J. Wang, Catalytic conversion of cellulose to 5-hydroxymethyl furfural using acidic ionic liquids and co-catalyst, Carbohydr. Polym. 90 (2012) 792–798.
- [16] Y. Yang, C. Hu, M.M. Abu-Omar, Conversion of carbohydrates and lignocellulosic biomass into 5-hydroxymethylfurfural using AlCl₃6H₂O catalyst in a biphasic solvent system, Green Chem. 14 (2012) 509–513.
- [17] X. Li, Y. Zhang, Q. Xia, X. Liu, K. Peng, S. Yang, Y. Wang, Acid-free conversion of cellulose to 5- (hydroxymethyl) furfural catalyzed by hot seawater, Ind. Eng. Chem. Res. 57 (2018) 3545–3553.
- [18] X. Bai, J.Y. Wang, N. Men, S.L. Zang, Degradation of microcrystalline cellulose to 5hydroxylmethylfurfural catalyzed by CrCl₃/[R₄N]ReO₄, Catal. Commun. 104

Z. Tang and J. Su

(2018) 37-40.

- [19] S. Suganuma, K. Nakajima, M. Kitano, D. Yamaguchi, H. Kato, S. Hayashi, M. Hara, Hydrolysis of cellulose by amorphous carbon bearing SO₃H, COOH, and OH groups, J. Am. Chem. Soc. 130 (38) (2008) 12787–12793.
- [20] D. Yamaguchi, K. Watanabe, S. Fukumi, Hydrolysis of cellulose by a mesoporous carbon-Fe₂(SO₄)₃/gamma-Fe₂O₃ nanoparticlebased solid acid catalyst, Sci. Rep. UK 6 (2016) 20327.
- [21] Z. Yang, R. Huang, W. Qi, L. Tong, R. Su, Z. He, Hydrolysis of cellulose by sulfonated magnetic reduced graphene oxide, Chem. Eng. J. 280 (2015) 90–98.
- [22] L. DaVià, C. Recchi, E.O. Gonzalez-Yañez, T.E. Davies, J.A. Lopez-Sanchez, Visible light selective photocatalytic conversion of glucose by TiO₂, Appl. Catal. B Environ. 202 (2017) 281–288.
- [23] S. Chu, L. Yang, X. Guo, L. Dong, X. Chen, Y. Li, X. Mu, The influence of pore structure and Si/Al ratio of HZSM-5 zeolites on the product distributions of α-cellulose hydrolysis, Mol. Catal. 445 (2018) 240–247.
- [24] L. Zhang, L. Tian, R. Sun, C. Liu, Q. Kou, H. Zuo, Transformation of corncob into furfural by a bifunctional solid acid catalyst, Bioresour. Technol. 276 (2019) 60–64.
- [25] M. Tyufekchiev, P. Duan, K. Schmidt-Rohr, S.G. Focil, M.T. Timko, M.H. Emmert, Cellulase-inspired solid acids for cellulose hydrolysis: structural explanations for high catalytic activity, ACS Catal. 8 (2018) 1464–1468.
- [26] P. Bhaumik, H.J. Chou, L.C. Lee, P.W. Chung, Chemical transformation for 5- hydroxymethylfurfural production from saccharides using molten salt system, ACS Sustain. Chem. Eng. 6 (2018) 5712–5717.
- [27] Y. Zhang, B. Li, Y. Wei, C. Yan, M. Meng, Y. Yan, Direct synthesis of metal-organic frameworks catalysts with tunable acid- base strength for glucose dehydration to 5hydroxymethylfurfural, Taiwan. J. Inst. Chem. Eng. 96 (2019) 93–103.
- [28] H. Liu, H. Wang, Y. Li, W. Yang, C. Song, H. Li, W. Zhu, W. Jiang, Glucose dehydration to 5-hydroxymethylfurfural in ionic liquid over Cr³⁺-modified ion exchange resin, RSC Adv. 5 (2015) 9290–9297.
- [29] Z. Xue, M.G. Ma, Z. Li, T. Mu, Advances in the conversion of glucose and cellulose to 5-hydroxymethylfurfural over heterogeneous catalysts, RSC Adv. 6 (2016) 98874–98892.
- [30] G. Sampath, K. Srinivasan, Remarkable catalytic synergism of alumina, metal salt and solvent for conversion of biomass sugars to furan compounds, Appl. Catal. Gen. 533 (2017) 75–80.
- [31] C. García-Sanchoa, I. Fúnez-Núnez, R. Moreno-Tost, J. Santamaría-González, E. Pérez-Inestrosa, J.L.G. Fierroa, P. Maireles-Torres, Beneficial effects of calcium chloride on glucose dehydration to 5- hydroxymethylfurfural in the presence of alumina as catalyst, Appl. Catal. B Environ. 206 (2017) 617–625.
- [32] C. Garcia-Sancho, I. Agirrezabal-Telleria, M. Guemez, P. Maireles-Torres, Dehydration of d-xylose to furfural using different supported niobia catalysts, Appl. Catal. B Environ. 152 (2014) 1–10.
- [33] C. Song, H. Liu, Y. Li, S. Ge, H. Wang, W. Zhu, Y. Chang, C. Han, H. Li, Production of 5-hydroxymethylfurfural from fructose in ionic liquid efficiently catalyzed by Cr (III)-Al₂O₃ catalyst, Chin. J. Chem. 32 (2014) 434–442.
- [34] S. You, N. Park, E. Park, M. Park, Partial least squares modeling and analysis of furfural production from biomass-derived xylose over solid acid catalysts, J. Ind. Eng. Chem. 21 (2015) 350–355.
- [35] R.M. Ravenelle, J.R. Copeland, W.G. Kim, J.C. Crittenden, C. Sievers, Structural changes of γ-Al₂O₃-supported catalysts in hot liquid water, ACS Catal. 1 (2011) 552–561.
- [36] Z. Tang, Y.Q. Liu, G.C. Li, X.F. Hu, C.G. Liu, Ionic liquid assisted hydrothermal fabrication of hierarchically organized γ-AlOOH hollow sphere, Mater. Res. Bull. 47 (11) (2012) 3177–3184.
- [37] Z. Tang, X.F. Hu, J.L. Liang, J.C. Zhao, Y.Q. Liu, C.G. Liu, Manipulating the morphology and textural property of γ-AlOOH by modulating the alkyl chain length of cation in ionic liquid, Mater. Res. Bull. 48 (6) (2013) 2351–2360.
- [38] A. Takagaki, J.C. Jung, S. Hayashi, Solid Lewis acidity of boehmite γ-AlO(OH) and its catalytic activity for transformation of sugars in water, RSC Adv. 4 (2014) 43785–43791.
- [39] T.F. Wang, M.W. Nolte, B.H. Shanks, Catalytic dehydration of C6 carbohydrates for the production of hydroxymethylfurfural (HMF) as a versatile platform chemical, Green Chem. 16 (2014) 548–572.
- [40] R.P. Swatloski, S.K. Spear, J.D. Holbrey, R.D. Rogers, Dissolution of cellulose with ionic liquids, J. Am. Chem. Soc. 124 (2002) 4974–4975.
- [41] M. Tan, L. Zhao, Y. Zhang, Production of 5-hydroxymethylfurfural from cellulose in CrCl₂/zeolite/BMIMCl system, Biomass Bioenergy 35 (2011) 1367–1375.
- [42] A. Gaikwad, S. Chakraborty, Mixing and temperature effects on the kinetics of alkali

metal catalyzed, ionic liquid based batchconversion of cellulose to fuel products, Chem. Eng. J. 240 (2014) 109–115.

- [43] C. Chiappe, M.J.R. Douton, A. Mezzetta, C.S. Pomelli, G. Assanelli, A.R. deAngelis, Recycle and extraction: cornerstones for an efficient conversion of cellulose into 5hydroxymethylfurfural in ionic liquids, ACS Sustain. Chem. Eng. 5 (2017) 5529–5536.
- [44] C.A. Emeis, Determination of integrated molar extinction coefficients for infrared absorption bands of pyridine adsorbed on solid acid catalysts, J. Catal. 141 (1993) 347–354.
- [45] K. Saravanan, B. Tyagi, S.R. Shukl, H.C. Bajaj, Esterification of palmitic acid with methanol over template-assisted mesoporous sulfated zirconia solid acid catalyst, Appl. Catal. B Environ. 172–173 (2015) 108–115.
- [46] Y. Han, L. Ye, X. Gu, P. Zhu, X. Lu, Lignin-based solid acid catalyst for the conversion of cellulose to levulinic acid using γ-valerolactone as solvent, Ind. Crops Prod. 127 (2019) 88–93.
- [47] D. Chiche, M. Digne, R. Revel, C. Chanéac, J. Jolivet, Accurate determination of oxide nanoparticle size and shape based on X-Ray powder pattern simulation: application to boehmite AlOOH, J. Phys. Chem. C 112 (2008) 8524–8533.
- [48] Y.G. Wang, P.M. Bronsveld, J.T.M. DeHosson, Ordering of octahedral vacancies in transition aluminas, J. Am. Ceram. Soc. 81 (6) (1998) 1655–1660.
- [49] X. Qi, M. Watanabe, T.M. Aida, R.L. Smith Jr., Fast transformation of glucose and Di-/Polysaccharides into 5- hydroxymethylfurfural by microwave heating in an ionic liquid/catalyst system, ChemSusChem 3 (2010) 1071–1077.
- [50] Y. Su, H.M. Brown, X. Huang, X. Zhou, J.E. Amonette, Z.C. Zhang, Single-step conversion of cellulose to 5- hydroxymethylfurfural (HMF), a versatile platform chemical, Appl. Catal. Gen. 361 (2009) 117–122.
- [51] L. Zhou, R. Liang, Z. Ma, T. Wu, Y. Wu, Conversion of cellulose to HMF in ionic liquid catalyzed by bifunctional ionic liquids, Bioresour. Technol. 129 (2013) 450–455.
- [52] X. Zhang, D. Zhang, Z. Sun, L. Xue, X. Wang, Z. Jiang, Highly efficient preparation of HMF from cellulose using temperature-responsive heteropolyacid catalysts in cascade reaction, Appl. Catal. B Environ. 196 (2016) 50–56.
- [53] K.Y. Nandiwale, N.D. Galande, P. Thakur, S.D. Sawant, V.P. Zambre, V.V. Bokade, One-Pot synthesis of 5-hydroxymethylfurfural by cellulose hydrolysis over highly active bimodal micro/mesoporous HZSM -5 catalyst, ACS Sustain. Chem. Eng. 2 (2014) 1928–1932.
- [54] X. Li, K. Peng, Q. Xia, X. Liu, Y. Wang, Efficient conversion of cellulose into 5hydroxymethylfurfural over niobia/carbon composites, Chem. Eng. J. 332 (2018) 528–536.
- [55] Q. Wu, G. Zhang, M. Gao, S. Cao, L. Li, S. Liu, C. Xie, L. Huang, S. Yu, A.J. Ragauskas, Clean production of 5-hydroxymethylfurfural from cellulose using a hydrothermal/biomass-based carbon catalyst, J. Clean. Prod. 213 (2019) 1096–1102.
- [56] Z. Cao, Z. Fan, Y. Chen, M. Li, T. Shen, C. Zhu, H. Ying, Efficient preparation of 5hydroxymethylfurfural from cellulose in a biphasic system over hafnyl phosphates, Appl. Catal. B Environ. 244 (2019) 170–177.
- [57] U. Tyagi, N. Anand, D. Kumar, Synergistic effect of modified activated carbon and ionic liquid in the conversion of microcrystalline cellulose to 5-hydroxymethyl furfural, Bioresour, Technol. 267 (2018) 326–332.
- [58] Y.B. Tewari, Thermodynamics of industrially-important, enzyme-catalyzed reactions, Appl. Biochem. Biotechnol. 23 (1990) 187–203.
- [59] R.S. Assary, P.C. Redfern, J.R. Hammond, J. Greeley, L.A. Curtiss, Computational studies of the thermochemistry for conversion of glucose to levulinic acid, J. Phys. Chem. B 114 (2010) 9002–9009.
- [60] A.S. Amarasekara, L.D. Williams, C.C. Ebede, Mechanism of the dehydration of Dfructose to 5-hydroxymethylfurfural in dimethyl sulfoxide at 150°C: an NMR study, Carbohydr. Res. 343 (2008) 3021–3024.
- [61] Y. Nishiyama, J. Sugiyama, H. Chanzy, P. Langan, Crystal structure and hydrogen bonding system in cellulose Iα from synchrotron X-ray and neutron fiber diffraction, J. Am. Chem. Soc. 125 (2003) 14300–14306.
- [62] Y. Nishiyama, P. Langan, H. Chanzy, Crystal structure and hydrogen-bonding system in cellulose Iβ from synchrotron X-ray and neutron fiber diffraction, J. Am. Chem. Soc. 124 (2002) 9074–9082.
- [63] I. Jiménez-Morales, A. Teckchandani-Ortiz, J. Santamaría-González, P. Maireles-Torres, A. Jiménez-López, Selective dehydration of glucose to 5-hydroxymethylfurfural on acidic mesoporous tantalum phosphate, Appl. Catal. B Environ. 144 (2014) 22–28.