

The influence of pore structure and Si/Al ratio of HZSM-5 zeolites on the product distributions of α -cellulose hydrolysis



Shuang Chu^{a,b,1}, Li'na Yang^{b,1}, Xingcui Guo^{a,*}, Linlin Dong^a, Xiufang Chen^a, Yaru Li^{a,b}, Xindong Mu^{a,*}

^a CAS Key Laboratory of Bio-based Materials, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China

^b School of Chemical and Environmental Engineering, Liaoning Shihua University, 1 Dandong Road, Fushun, Liaoning 113001, China

ARTICLE INFO

Article history:

Received 27 May 2017

Received in revised form

22 November 2017

Accepted 22 November 2017

Available online 22 December 2017

Keywords:

Hydrolysis

α -Cellulose

HZSM-5

Si/Al ratio

Ultrasonic

ABSTRACT

The catalytic behavior of a series of MFI catalysts with different Si/Al ratio (25–300) in the direct aqueous-phase hydrolysis of α -cellulose was studied. The effects ultrasonic pretreatment time, ZnCl₂ content, zeolite pore structure and acid-basic properties on catalyst activity and products distribution were systematically investigated. The results indicated that HZSM-5 with lower Si/Al ratio was beneficial for production of glucose and LA from α -cellulose. Ultrasonic pretreatment could decrease the degree of crystallinity and polymerization of α -cellulose, enhance the accessibility of acid sites and ZnCl₂ to the loosened amorphous regions of α -cellulose in water, and improve the hydrolysis efficiency of α -cellulose. The desilicated ZSM-5 (HZSM-5-DS(0.2)) showed much higher catalytic activities as compared to commercial ZSM-5 and α -cellulose conversion reached 76.5% over HZSM-5-DS(0.2) at 200 °C. Catalytic conversion of α -cellulose consisted of at least three important parallel reactions under the present hydrothermal conditions and a plausible pathway was proposed. Effective control of these reactions would be helpful to further maximize the target product yield during the catalytic conversion of α -cellulose.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Considering the depletion of fossil resources and global warming issues, investigations of alternative energy strategies are of importance. In this respect, biomass as sustainable and renewable raw materials was considered to be one of the most potential substitutes for the production of liquid renewable fuels and chemicals to displace petroleum in the next few years [1–3]. Cellulose, a natural polymer consisting of glucose units, were considered as a versatile feedstock for the production of interesting bulk chemicals by the acid-catalyzed hydrolysis reaction [4,5]. During hydrolysis, the β -(1,4)-glycosidic bonds of cellulose are cleaved to give glucose, which can be converted further to various organic (bulk) chemicals.

Hydrolysis of cellulose has been studied previously using various types of acidic catalysts including mineral acids or solid acids [6–11]. While homogeneous catalytic processes often suffered some disadvantages, such as difficult separation and recovery

of catalysts, serious environmental pollution and equipment corrosion. Therefore, various solid acid catalysts were developed to hydrolyze cellulose to value-added chemicals in recent years [12]. Among the known solid acid catalysts for the hydrolysis of cellulose, zeolites has proven to be the best choices, owing to their tunable acidities, special pore structure, excellent shape-selectivities [13,14], easily separated from the reaction mixture, and reused in repeated reactions. In recent years, several zeolites with different structure, such as microporous zeolites (H-USY, H β , H-MOR, HZSM-5 and SAPO-34) and mesoporous molecular sieves (Al-MCM-41 and Al-SBA-15) have been employed for cellulose hydrolysis using water or ionic liquids (ILs) as solvent [15,16].

In 2008, Onda and co-workers found that the H β and HZSM-5 zeolites with high Si/Al ratios showed higher catalytic activities for the production of glucose from cellulose hydrolysis. However, the yield of glucose was only of 12% [17]. Recently, Zhao found that HY zeolite with Si/Al molar ratio of 5 showed the highest yield of glucose 36.9% using [C₄mim]Cl as solvent under microwave irradiation [18]. In this context, Zhang and co-workers investigated a variety of H-type zeolites (HY, H β , HZSM-5 and SAPO-34) for cellulose hydrolysis and found that the yield to glucose was about 50.0% on HY catalyst under [Bmim]Cl [19]. However, the expensive cost

* Corresponding authors.

E-mail addresses: guoxc@qibebt.ac.cn (X. Guo), muxd@qibebt.ac.cn (X. Mu).

¹ These authors contributed equally.

and high viscosity of ILs hamper its commercialized application. Compared with ILs, water as an economic and environment friendly solvent [20], was used as cellulose hydrolysis medium [21]. However, cellulose and solid acids are typically not soluble in water, so the hydrolysis of cellulose can only proceed at the interface of solid catalyst under water. To achieve a high conversion of cellulose, large pore diameter and high external area of solid materials are favorable for cellulose hydrolysis catalysts. Recently, Zhou reported hierarchical H-USY zeolite (H-USY-meso) with meso/micropores and large external area for the hydrolysis of hemicelluloses [22]. It was found that meso/macropores and large external area benefited the improvement of activity and selectivity for reducing sugars. Unfortunately, the acid strength and amount of H-USY meso decreased sharply with introduction of meso/macropores by acid-dealumination. On the other hand, the low selectivity makes the separation and purification of the intermediate products a big problem.

Previous studies have shown that reaction pathway for the hydrolysis of cellulose was complex, including a series of consecutive and parallel reactions, such as hydrolysis, dehydration and hydrogenation. Cellulose hydrolytic conversion to different products depending on the catalyst and reaction condition. Therefore, development of effective solid acid catalysts with suitable acidity and pore structure for hydrolysis of cellulose to obtain high selectivity for target product is still a major challenge. In order to design of catalysts rationally and gain better insights into the reaction pathways of catalytic conversion of cellulose, the depolymerization of α -cellulose over zeolites containing HZSM-5 with different Si/Al ratios and modified HZSM-5 by desilication or dealumination are investigated systematically in this work.

The effect of pore structure and acidity of zeolites, ZnCl₂ content and ultrasonic pretreatment on products distribution of α -cellulose hydrolysis are also demonstrated. By combination of XRD, physisorption, FT-IR, NH₃-TPD characterizations and element analysis, we provide new insights into the behavior of zeolite for α -cellulose hydrolysis in water. A hydrolysis pathway is proposed based on the reactivity and products distribution observed on these catalysts.

2. Experimental

2.1. Materials

α -cellulose (MW = 162) and 5-HMF were purchased from Sigma-Aldrich. Glucose and other chemicals were obtained from Aladdin Industrial Inc.; HZSM-5 zeolites with various Si/Al ratios (25, 60, 120 and 300, respectively) were obtained from Catalyst Factory of Nankai University, named as "HZSM-5(Si/Al ratio)".

2.2. Catalysts preparation

Alkali-treatment of the HZSM-5 zeolites with Si/Al ratio about 25 was performed at 65 °C for 60 min with NaOH solution at a concentration of 0.2 and 0.4 mol/L with the mass ratio of 1: 30. Finally, 1 g solid products were exchanged with 15 mL 0.2 mol/L NH₄NO₃ solution at 85 °C and washed with a large amount of deionized water, repeatedly. After drying, the samples in NH₄-form were calcined in static air at 550 °C for 5 h (heating rate of 1 °C/min) to convert them into H-form. The samples treated with 0.2 and 0.4 mol/L of NaOH are denoted as HZSM-5-DS(0.2) and HZSM-5-DS(0.4), respectively.

The acid dealumination of zeolite HZSM-5 with Si/Al ratio of 25 was carried out under reflux for 10 h with 0.4 and 0.8 mol/L aqueous solution of HCl, the sample was separated by filtration and then washed with deionized water extensively. The obtained solid prod-

uct was dried at 100 °C and calcined at 550 °C for 5 h. The obtained samples are referred to as HZSM-5-DA(0.4) and HZSM-5-DA(0.8), respectively.

In this work, the ultrasonic-treatment of the α -cellulose was carried out in Ultrasonic Generator (KH100E, China) at a power of 750 W and a frequency of 20 kHz for 0, 1 and 2 h, respectively. The obtained samples were denoted as C-U-0, C-U-1 and C-U-2, respectively.

2.3. Catalyst characterization

X-ray diffraction (XRD) patterns of samples were carried out with a Bruker D8 Advance X-ray diffractometer (Bruker, Germany) using Cu K α source ($\lambda = 0.154$ nm) in a 2 θ range from 5° to 60° with a scan speed of 10°/min. Nitrogen adsorption–desorption experiments were measured on a Micromeritics ASAP 2020 surface area and porosity analyzer to characterize BET surface area and textural properties of catalysts. The total surface area and micropore volume was calculated according to the BET and the t-plot method, respectively. NH₃-temperature-programmed desorption (NH₃-TPD) was conducted on a Micromeritics Auto II 2920 (USA) to measure the numbers of acidic sites and acid strengths for these catalysts with a heating rate of 10 °C/min from 25 °C to 900 °C. FT-IR spectra were recorded with FT-IR spectrometer (Nicolet 6700 spectrometer, America). The IR-pyridine adsorption was obtained on a Nicolet 6700 spectrometer to study the nature of acid. The catalyst samples were placed into a fine powder and pressed into self-supported discs. The discs were placed in the centre of IR cell. Firstly, the sample discs were heated to 100 °C at 10 °C/min under vacuum and kept for 1 h. Then, the excess pyridine in the IR cell was removed. After each step, spectra were recorded at room temperature.

2.4. Catalytic hydrogenolysis reaction

A general procedure to conduct the α -cellulose hydrolysis was the same as reported before [23,24], after 0.4 g catalyst, 0.25 g α -cellulose and 20 mL water were loaded into a 50 mL stainless-steel autoclave, the reactor was purged four times with nitrogen to remove air, pressurized to 1 MPa nitrogen pressure at room temperature and finally programmed to 200 °C for 2 h at a stirring speed of 800 RPM. After reaction, the reactor was cooled down to room temperature as soon as possible. The product mixture was centrifuged. The supernatant was filtered through a 0.45 μ m membrane before analysis. The solid residual was dried at 80 °C for overnight. The conversion of α -cellulose was calculated by the weight difference in the solid before and after reaction. Reactant conversion was defined as follows:

$$\text{Conversion (\%)} = \frac{(\text{mass of inlet cellulose} - \text{mass of outlet cellulose})}{\text{mass of inlet cellulose}} * 100\%$$

Concentration changes of main products such as glucose, 5-HMF, LA and FA were quantitated by external standard method. 5-HMF was quantified using a Waters HPLC with an UV detector at 284 nm and a SB-C18 column (4.8 × 150 mm). The mobile phase was a mixture of methanol and water (20: 80, v/v) with a flow rate of 0.7 mL/min at 35 °C. Glucose, LA and FA were analyzed by a HPLC system (Agilent 1200) equipped with RI detector and an Aminex HPX-87H column (Bio-Rad, 7.8 × 300 mm), using 5 mM H₂SO₄ as eluent with a flow rate of 0.5 mL/min at 55 °C.

The substrate used in this study was α -cellulose and the crystallinity index (CrI) [25] was estimated by XRD analysis according

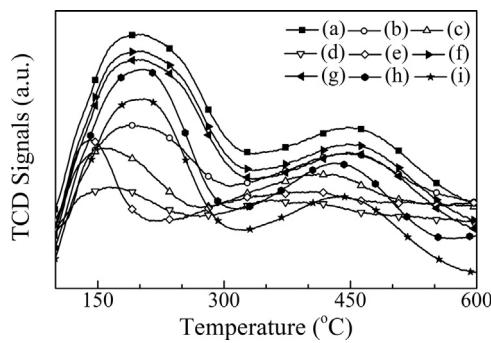


Fig. 1. NH₃-TPD profiles of various MFI zeolites: (a) HZSM-5(25); (b) HZSM-5(60); (c) HZSM-5(120); (d) HZSM-5(300); (e) Silicalite-1; (f) HZSM-5-DA (0.4); (g) HZSM-5-DS (0.2); (h) HZSM-5-DS (0.4); (i) HZSM-5-DA (0.8).

to the empirical method developed by Segal and coworkers using the following equation [26–28]:

$$I_{\text{CrI}} = \frac{I_{002} - I_{\text{am}}}{I_{002}}$$

Where I₀₀₂ is the maximum intensity (in arbitrary units) of the 002 lattice diffraction and I_{am} is the intensity diffraction (in the same units) at $2\theta = 18^\circ$.

3. Results and discussion

3.1. Characterization of the catalysts

3.1.1. Surface acid properties (NH₃-TPD)

The catalytic activity during the dehydration of cellulose depends on the nature of surface acidic properties of the used catalysts. NH₃-TPD is a typical technology to distinguish distribution and determine the amount of acidic sites over solid catalysts [29,30]. NH₃-TPD profiles for different HZSM-5 samples are shown in Fig. 1, and the corresponding acid amount of these catalysts measured by temperature-programmed desorption of NH₃ method are listed in Table 1. All the samples show two main peaks:

a low-temperature desorption peak centered at around 150–300 °C assigned to NH₃ chemisorbed on weak acid sites or non-acidic sites [31], and a high-temperature desorption peak observed above 400 °C generally attributed to the desorption of NH₃ from strong Brønsted and Lewis sites, which plays important role for cellulose conversion.

As shown in Fig. 1, the profiles of unmodified zeolites are remarkably different from each other. Both the two desorption peaks slightly move to a lower temperature, and the peak area decreases with increasing Si/Al ratio, which is in line with the number of aluminum atoms. The NH₃ desorption profiles for dealuminated HZSM-5 are analogous to those of unmodified HZSM-5 zeolites, which shows similar strength in acidity, but different in acid amount.

The desorption temperature of HZSM-5-DS(0.2) catalyst, whether low temperature or high temperature peak, is both higher than HZSM-5-DA(0.4) sample obviously. The amount of acid sites calculated from the NH₃-TPD curves are depicted in Table 1. It can be found that the total acid amounts of HZSM-5-DS(0.2) has no obvious changes compared with HZSM-5(25) catalyst. According to the previous works [32], a few extra-framework Al species contributed to the Lewis acidity were produced inevitably during alkali treatment. As can be seen from the results reported in Fig. 1, The desorption temperatures of NH₃ corresponding to moderate and strong acid strengths, shift to lower temperature range for dealuminated HZSM-5-DA(0.4) catalyst. As shown in Table 1, the acidity of HZSM-5-DA(0.4) (1.22 mmol g⁻¹) catalyst is slightly decreased

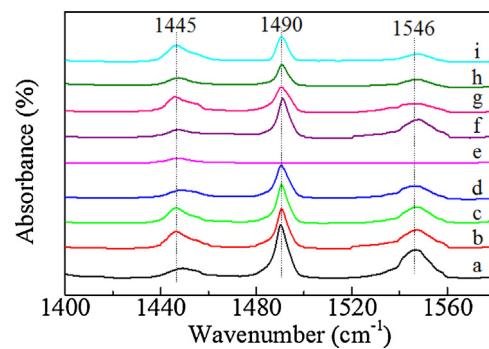


Fig. 2. Py-IR spectra of different catalysts: (a) HZSM-5(25); (b) HZSM-5(60); (c) HZSM-5(120); (d) HZSM-5(300); (e) Silicalite-1; (f) HZSM-5-DA (0.4); (g) HZSM-5-DS (0.2); (h) HZSM-5-DS (0.4); (i) HZSM-5-DA (0.8).

than the HZSM-5(25) (1.35 mmol g⁻¹) catalyst due to the partial removal of Al atoms (Si-OH-Al) that occurs simultaneously with the preferential removal of Si atoms (Si-OH-Si) from the HZSM-5 framework.

NH₃-TPD patterns of the dealuminated HZSM-5-DA(0.8) zeolites reveal that the high-temperature TPD peak decreased after the dealumination process indicating that part of framework aluminum species are removed during the treatment with HCl solution. For desilicated HZSM-5(0.4) zeolites, the total amount of acid sites decrease to 1.02 mmol g⁻¹. Both the weak and strong acid sites in the parent HZSM-5(25) zeolites decreased during the desilication process (Fig. 1h). As presented in Fig. 1, the TPD profile of silicalite-1 shows one peak at lower temperature about 170 °C, suggesting that weak acid sites mainly exist over silicalite-1, the lower acidity of silicalite-1 is also further supported by Py-FTIR results.

3.1.2. Py-FTIR

For characterizing the acidity on the surface of HZSM-5 catalysts, the samples were saturated for 2 h at 150 °C in a pyridine stream (mL/min), then cooled down to ambient temperature and a subsequent purged for ca. 15–30 min until a constant baseline level was attained. As shown in Fig. 2, the band at 1445 cm⁻¹, arising due to the ν(C–C) vibration of pyridine adsorbed at the Lewis acid sites, can be assigned to extra-framework AlOH species or Brønsted site dehydration [33]. The band at 1546 cm⁻¹, generated from the ν(C–C) vibration of pyridine adsorbed at the Brønsted acid sites, is associated to tetra-coordinated Al atom of zeolite framework [34]. The band in this spectrum at 1490 cm⁻¹ are ascribed to both Lewis and Brønsted acid sites [35]. Whereas the intensity of these three bands for different HZSM-5 samples decrease progressively with increasing Si/Al ratio. Therefore, the data on acid site distribution given in Table 1 clearly reveals that the total acid amount of HZSM-5 zeolites decreases with increasing Si/Al ratios, which is in agreement with NH₃-TPD results described above.

In the case of silicalite-1 (curve e), mainly one bands at 1445 cm⁻¹ corresponding to the adsorption of pyridine at Lewis acid site is observed and its intensity is smaller than HZSM-5 samples. The bands assigned to Brønsted acid sites or Brønsted and Lewis acid sites disappear almost completely for silicalite-1. The spectra for dealuminated (HZSM-5-DA(0.4) and HZSM-5-DA(0.8)) and desilicated (HZSM-5-DS(0.2) and HZSM-5-DS(0.4)) samples in the region are similar as the spectra of HZSM-5(25), indicating that dealumination or desilication of HZSM-5 is not accompanied by destruction of the zeolite framework.

3.1.3. FTIR

The FTIR spectra of HZSM-5 zeolites are shown in Fig. 3. The bands near 794, 1098 and 1220 cm⁻¹ are characteristic of SiO₄ tetrahedron units [36]. The strong band in the region

Table 1
NH₃-TPD and Py-IR results of various MFI samples.

Catalysts	Acid sites from NH ₃ -TPD (mmol g ⁻¹) ^a			Acid sites from Py-IR (mmol g ⁻¹) ^b		
	Weak	Strong	Total	L acid	B acid	L/B
HZSM-5(25)	0.86	0.49	1.35	0.10	0.49	0.20
HZSM-5(60)	0.71	0.38	1.09	0.15	0.31	0.48
HZSM-5(120)	0.49	0.30	0.79	0.14	0.19	0.74
HZSM-5(300)	0.24	0.11	0.35	0.06	0.12	0.50
Silicalite-1	0.65	—	0.65	0.06	—	—
HZSM-5-DA(0.4)	0.81	0.41	1.22	0.09	0.45	0.20
HZSM-5-DS(0.2)	0.78	0.34	1.14	0.14	0.21	0.67
HZSM-5-DA(0.8)	0.66	0.30	1.08	0.07	0.41	0.17
HZSM-5-DS(0.4)	0.75	0.37	1.02	0.13	0.25	0.52

^a Acid sites density is calculated from NH₃-TPD (weak acid 100–350 °C, strong acid 350–600 °C).

^b Density of the acid sites, assorted according to the acidic type, determined by Py-IR, L/B, the ratio of density of L acid sites to B acid sites.

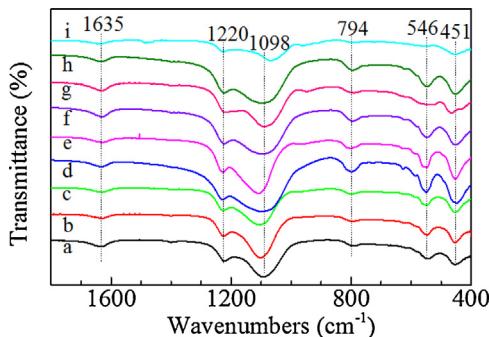


Fig. 3. FTIR spectra for various catalysts, transmission during 4000–400 cm⁻¹: (a) HZSM-5(25); (b) HZSM-5(60); (c) HZSM-5(120); (d) HZSM-5(300); (e) Silicalite-1; (f) HZSM-5-DA (0.4); (g) HZSM-5-DS (0.2); (h) HZSM-5-DS (0.4); (i) HZSM-5-DA (0.8).

1000–1300 cm⁻¹ is assigned to the internal vibration of SiO₄, AlO₄ tetrahedra for HZSM-5. The band around 1098 cm⁻¹ is attributed to the internal asymmetric stretching vibration of Si–O–T linkage [37]. As shown in Fig. 3, the asymmetric stretching vibration peaks at 1220 cm⁻¹ generally shift to higher wavenumbers with increasing Si/Al ratio. This shift is due to the slightly lower mass of aluminum compared to that of silicon. The band near 794 cm⁻¹ is assigned to the symmetric stretching of the external linkages, and the strong band near 546 cm⁻¹ is attributed to the double five-ring lattice vibration of the external linkages. The band at around 451 cm⁻¹ is due to the T–O bending vibrations of the SiO₄ and AlO₄ internal tetrahedra. The bands around 546 and 451 cm⁻¹ are characteristic of the HZSM-5 crystalline structure.

3.1.4. XRD

α-Cellulose is a highly crystalline polymer of d-anhydroglucopyranose units joined together in long chains by β-1,4-glycosidic bonds [38], which makes it indispersible in most solvents and thus notoriously resistant to hydrolysis. A physical pretreatment such as ultrasonication is essential for breaking down the hydrogen bonds and enhancing accessibility of active sites of catalyst to the loosened amorphous regions of α-cellulose.

The effect of ultrasound treatment on the crystallinity of α-cellulose is investigated through XRD analysis (Fig. 4). It can be seen from Fig. 4 that all the XRD patterns present five crystalline peaks (101, 10-1, 021, 002 and 040), indicating that the structure of α-cellulose after ultrasound is not disrupted significantly. Although raw and pretreated α-cellulose have similar diffraction patterns, some changes in the peak intensity occur after pretreatment. In order to qualify the changes of α-cellulose, the crystallinity index (ICR) is calculated from Eq. (3) according to the conventional peak intensity method [39]. The ICR decreases from 0.750

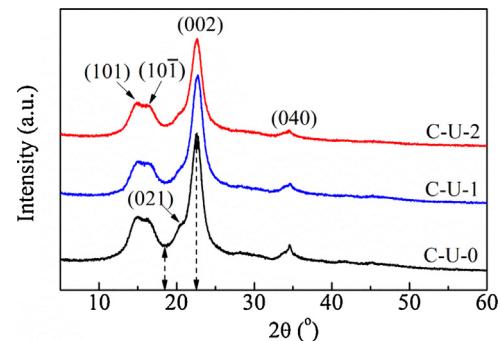


Fig. 4. The XRD patterns of α-cellulose before and after ultrasonic treatment.

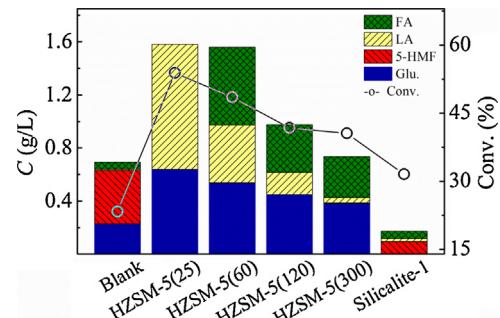


Fig. 5. α-Cellulose hydrolysis performance over MFI zeolites with various Si/Al ratios. Reaction conditions: 0.25 g α-cellulose, 20 mL H₂O, catalyst charge 0.4 g, 200 °C, 800 RPM.

(C-U-0) to 0.515 (C-U-1) after one hour ultrasonic pretreatment. With prolonging ultrasonic treatment time to 2 h, the ICR is further decreased to 0.364, indicating that ultrasound treatment with appropriate ultrasonic time is an efficient method for decreasing crystallinity of α-cellulose.

3.2. Catalytic activity studies

3.2.1. Effects of Si/Al ratio of HZSM-5 on α-cellulose hydrolysis

As shown in Fig. 5, the conversion of α-cellulose is only 23.4% without using catalyst, which can be greatly improved after adding the HZSM-5 or silicalite-1 catalyst. The hydrolysis activity of HZSM-5 zeolites is decreased from 63.9% to 41.6% with Si/Al ratios increasing from 25 to 300. Compared with a series of HZSM-5 catalysts, only about 31.6% α-cellulose conversion is achieved on pure silica silicalite-1 catalyst. Above results indicate that the acid density of catalysts play an important role in α-cellulose hydrolysis. The acid properties of different MFI zeolites are influenced by their Si/Al ratios of frameworks or structure. According to the results of

$\text{NH}_3\text{-TPD}$ and Py-FTIR as shown in Table 1, it can be found that both the total acid amounts and Brønsted acid sites of different MFI zeolites decline with increasing Si/Al ratios. The amounts of surface Brønsted acid sites decrease from 1.35 to 0.35 (mmol of NH_3) (g of zeolite^{-1}) with Si/Al ratio increasing from 25 to 300, whereas the Lewis acid sites almost remain unchanged. There is no adsorption band characteristic of Brønsted acid sites at 1546 cm^{-1} is observed from sample silicalite-1, indicating that Brønsted acid is more favorable for the hydrolysis of β -1,4 glycosidic bonds of cellulose [40].

It can be seen from Fig. 5, the products for α -cellulose conversion are mainly consisted of glucose, 5-hydroxymethylfurfural (5-HMF), levulinic acid (LA) and formic acid (FA). The undesired minor byproducts are not quantified in this work. 0.23 g L^{-1} of glucose is produced in the absence of catalyst under the same reaction conditions. This value can be increased sharply after adding HZSM-5 catalysts, but it is observed to decrease from 0.64 to 0.38 g L^{-1} as Si/Al ratio increases from 25 to 300. The results suggest that glucose yield is strongly influenced by the Si/Al ratios of HZSM-5 zeolites and lower Si/Al ratio is beneficial to the formation of glucose. The concentration to 5-HMF is about 0.40 g L^{-1} with no catalyst. It is worth noting that after adding HZSM-5 catalysts, 5-HMF concentration substantially decreases to below 0.01 g L^{-1} . When with silicalite-1 as catalyst, the concentration of 5-HMF increases to over 0.09 g L^{-1} under identical reaction conditions. Compared with blank experiment, cellulose conversion is greatly improved after adding silicalite-1 catalyst, but the total concentration of products is very low, which may be due to the fact that the produced 5-HMF is further transformed into humins or carbon dioxide during the reaction. The textural properties and of all the MFI samples, are listed in Table S1 (see Supporting information). The main differences between HZSM-5 and silicalite-1 are their framework component and acidity types due to their similar properties (BET surface area and total pore volume). It suggests that 5-HMF yield strongly depends on the acid strength as well as types of catalysts. The type and amount of surface acid for all the catalysts are determined by the method of FT-IR spectroscopy of pyridine adsorption (Fig. 1) and $\text{NH}_3\text{-TPD}$ technique (Fig. 3). As listed in Table 1, only surface Lewis acid sites are presented on the surface of silicalite-1 from FTIR-Pyridine analysis. After incorporation with aluminium, both Lewis and Brønsted acid sites are detected on the surface of series HZSM-5 samples. So it can be concluded that 5-HMF may further convert into LA and FA by Brønsted acid site.

The concentrations of LA and FA, known as products derived from rehydration of 5-HMF, decrease with the increase of Si/Al ratio over HZSM-5 zeolites. In the meanwhile, the decreasing rate of LA concentration is more faster than that of FA. Highest concentration of LA (0.94 g L^{-1}) is obtained when HZSM-5(25) is used (Fig. 5), followed by the Si/Al ratio of 60 (0.43 g L^{-1}), 120 (0.17 g L^{-1}) and 300 (0.04 g L^{-1}), respectively. The concentration of LA decreases to about 0.01 and 0.02 g L^{-1} either with silicalite-1 or without catalyst. The results show that low Si/Al ratio (higher acid concentration) is beneficial to the conversion of 5-HMF to LA. This may be due to the increased availability of Brønsted acid sites required for the rehydration of 5-HMF.

3.2.2. Catalytic activity of post-treated HZSM-5 samples

Various crystalline microporous zeolites [19] were developed to hydrolyze α -cellulose to sugars in recent years due to their high ion-exchange capacity, strong acidity and high stability. Despite above advantages, the hydrolysis of α -cellulose can only proceed at the interface of zeolites and cellulose, due to the low solubility of α -cellulose in water and small pore size (usually less than 1 nm) of zeolites. It was found that meso/macropores and large external area benefited the improvement of activity and

selectivity for reducing sugars. So, considerable efforts have been devoted to the development of mesoporous materials that have a zeolitic framework, with the aim of combining the advantages of the high acidity of the crystalline zeolite and the facile diffusion of bulky molecules in a mesoporous material. Zhou et al. [41] recently reported that hierarchical H-USY zeolite (H-USY-meso) with meso/micropores and large external area for the hydrolysis of hemicelluloses. It was found that meso/macropores and large external area remarkably improved the activity for α -cellulose hydrolysis. Unfortunately, the acid strength and stability of H-USY-meso decreased sharply with introduction of meso/macropores by acid-dealumination. Srivastava et al. recently reported that MFI zeolite with a mesoporous/microporous hierarchical structure (MeMFI zeolite) showed remarkably improved resistance to the deactivation of the catalytic activities in various reactions [42]. So, in this study, various H-ZSM-5 zeolites with different Si/Al ratios or pore structures introduced by dealumination or desilication treatment are used as catalysts for α -cellulose hydrolysis.

As shown in Fig. S1 (see Supporting information), there is no pronounced structure difference between parent and modified HZSM-5 zeolites. Only diffraction peaks belong to MFI structured zeolite can be found and, indicating that no new phase formed after the acid or basic-treatment. The alkali-treated zeolite of HZSM-5-DS(0.2) with Si/Al ratio of 21 has crystallinity similar to that of the parent zeolite, and the relative crystallinity decreases slightly after alkali-treatment. The XRD peak intensity of HZSM-5-DA(0.4) (Si/Al = 31) has no obviously change after 0.4 mol/L HCl treatment. However, increasing the HCl acid solution concentration to 0.8 M , its crystallinity decreases to 93.6% due to Al extraction from the framework.

N_2 physical adsorption/desorption measurements for parent and post-treated HZSM-5 samples are also carried out, and the results are shown in Fig. S2 (see Supporting information). The parent HZSM-5 and dealuminated H-ZSM-5 samples show type I isotherms indicating their purely microporous nature. Both HZSM-5-DS(0.2) and HZSM-5-DS(0.4) show typical IV N_2 adsorption-desorption isotherm due to the presence of mesopores with narrow distribution. The surface area of HZSM-5-DS(0.2) is $385\text{ m}^2\text{ g}^{-1}$, higher than the parent HZSM-5(25) catalyst ($360\text{ m}^2\text{ g}^{-1}$). The mesopore volumes of HZSM-5-DS(0.2) ($0.16\text{ cm}^3\text{ g}^{-1}$) is much larger than that of parent HZSM-5 catalyst ($0.02\text{ cm}^3\text{ g}^{-1}$) and HZSM-5-DA(0.4) sample ($0.04\text{ cm}^3\text{ g}^{-1}$) (see Supporting information, Table S1).

The $\text{NH}_3\text{-TPD}$ profiles of the post-treated HZSM-5 samples are also shown in Fig. 1 and two distinct NH_3 desorption peaks in the range below 500°C are observed. The desorption peak in the range of $0\text{--}300^\circ\text{C}$ is due to NH_3 bound to weak acid sites, and the high temperature desorption peak in the range of $300\text{--}500^\circ\text{C}$ is caused by NH_3 desorption from strong acid sites (Brønsted and Lewis acid sites). The numbers of both the strong and weak acid sites in HZSM-5-DA(0.4) and HZSM-5-DS(0.2) samples are similar with those in the parent HZSM-5, indicating that the acidity of modified HZSM-5 samples after low concentration acid or alkali-treatment has no obvious change. Compared to HZSM-5, the total amount of acid of HZSM-5-DA(0.8) is 1.08 mmol g^{-1} which is 80% of the total acid content of HZSM-5(25) zeolite. The acid amount in HZSM-5-DS(0.4) is about 76% of the HZSM-5(25)'s total acid quantity, which is in good agreement with earlier report regarding the acidity of hierarchical porous zeolites by Suzuki et al. [43].

The main product distributions of the α -cellulose hydrolysis reaction at 200°C for all the catalysts are given in Table 2. As shown in Table 2, the desilicated HZSM-5-DS(0.2) exhibits higher α -cellulose hydrolysis activity (76.5%) than the parent HZSM-5(25) (63.9%). Compared to HZSM-5-DS(0.2), the conversion of α -cellulose decreases to 68.2% over HZSM-5-DS(0.4). It is found that HZSM-5(25) catalysts treated with different con-

Table 2

Product distributions of α -cellulose hydrolysis over the parent HZSM-5 and post-treated samples.

Entry	Catalysts	Conversion (%)	Product distribution (g L^{-1})			
			Glucose	HMF	LA	FA
1	HZSM-5-DA(0.4)	62.4	0.28	0.11	0.01	0.00
2	HZSM-5-DS(0.2)	76.5	0.35	0.15	0.07	0.02
3	HZSM-5-DA(0.8)	59.7	0.31	0.06	0.22	0.08
4	HZSM-5-DS(0.4)	68.2	0.41	0.23	0.26	0.01
5	Blank	23.4	0.23	0.40	0.01	0.06
6	Blank ^a	44.1	0.15	0.45	0.16	0.09
7	HZSM-5(25)	63.9	0.64	0.00	0.94	0.20
8	HZSM-5(25) ^b	84.2	0.70	0.03	3.24	1.27
9	HZSM-5(25) ^c	66.2	0.72	0.01	2.05	0.71
10	HZSM-5(25) ^d	11.5	0.18	0.11	0.03	0.07

Reaction conditions: 0.25 g α -cellulose, 0.4 g catalyst, 20 mL total volume, 200 °C, 2 h. ^{a,b} 0.2 g ZnCl_2 ; ^c 0.3 g ZnCl_2 ; ^d 0.4 g ZnCl_2 .

centrations of HCl solution show almost the same α -cellulose conversion (Table 2, entries 1 and 3) at the reaction temperature of 200 °C. This may be due to the acid sites in microporous HZSM-5 zeolites are mainly located at the channels of the zeolite. Due to the small size of the channel of HZSM-5(25), α -cellulose can hardly diffuse into the channels and the hydrolysis of α -cellulose in water can only proceed at the external surface or in meso/macropore of zeolite. At the same time, the size of glucose molecular (0.50 nm × 0.57 nm × 0.58 nm) is too large to enter the micropores of HZSM-5 [44]. So glucose concentration is high and small amounts of LA and FA are detected over HZSM-5(25). Almost no 5-HMF is detected using HZSM-5 with different Si/Al molar ratios in the range of 25–300 as catalysts, indicating that the formed 5-HMF is unstable and can be easily hydrolyzed to LA and FA catalyzed by the acid sites in the micropores. When using desilicated HZSM-5-DS(0.2) as catalyst, large external surface area and mesopore are beneficial for α -cellulose and glucose conversion. The catalytic activity of HZSM-5-DA(0.4) zeolite is lower than HZSM-5-DS(0.2) with respect to conversions of α -cellulose and glucose. This may be due to α -cellulose and glucose conversions are mainly catalyzed by Brønsted acids of the framework tetrahedral Al species and the diffusion limitation of the micro-sized channels of HZSM-5-DA(0.4) cause incomplete of α -cellulose or glucose into the micropores.

3.2.3. Effect of ZnCl_2 on α -cellulose hydrolysis

It was recently reported that a highly concentrated ZnCl_2 aqueous solution (>60 wt%) was used as an efficient reaction medium for transforming lignocellulosic biomass and chitin biomass into value-added fine chemicals [45], such as 5-HMF and isosorbide, under relatively mild conditions. However, it is a challenge to separate the target products from the highly concentrated ZnCl_2 solutions and usually high energy consumption is needed during this process. On the other hand, compared with aqueous solution, recycling of this solvent is difficult due to the formation of excess amounts of undesired by-products such as humins or other polymers in ZnCl_2 solution is high, which leads to low product selectivity and yield in the next run. Whereas, high concentration of Zn^{2+} ions in reaction solutions can bring some difficulty for the qualitative and quantitative analysis of main products using ^1H NMR or HPLC.

So in this work, the hydrolysis of α -cellulose is promoted by dilute ZnCl_2 even its concentration below 0.2 mol/L. So, ZnCl_2 plays a completely different role in the degradation of α -cellulose biomass. Hence, a set of experiments are conducted varying ZnCl_2 amount in order to investigate how the ZnCl_2 contents influence the conversion of α -cellulose and the products distribution including 5-HMF and LA in water.

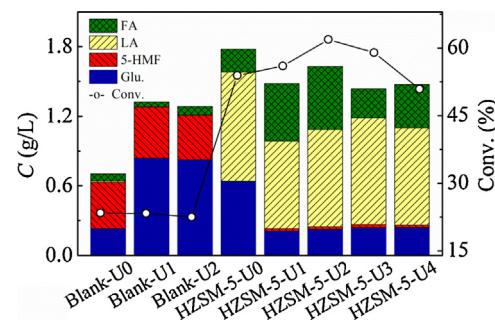
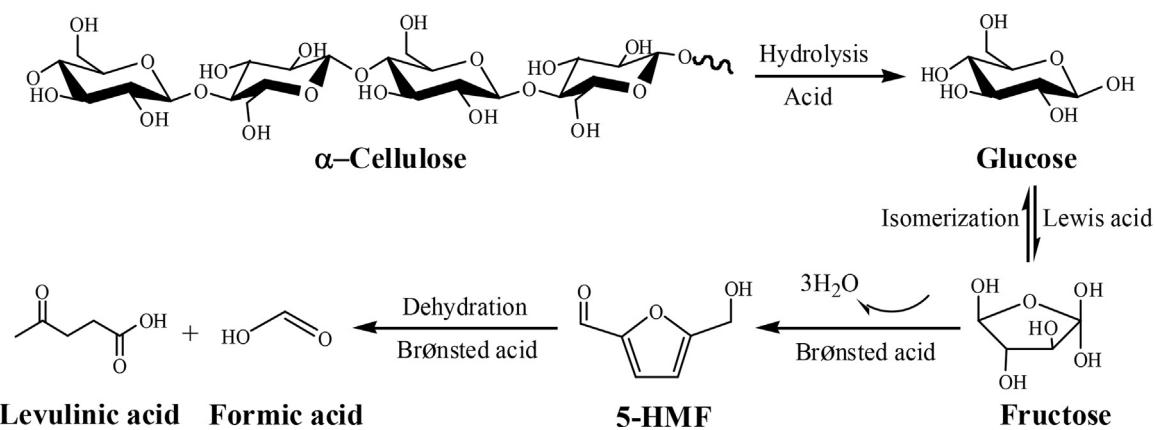


Fig. 6. Effect of ultrasonic pretreatment on α -cellulose hydrolysis. Reaction conditions: 0.25 g α -cellulose, 20 mL H_2O , 0.4 g HZSM-5(25), 200 °C, 800 RPM.

Table 2 presents the effect of ZnCl_2 content ranging from 0 to 0.4 g on catalytic results for α -cellulose hydrolysis over HZSM-5(25) catalyst. It is found that suitable amounts of ZnCl_2 can improve α -cellulose conversion obviously, implying that ZnCl_2 is an effective promoter for α -cellulose hydrolysis. Total products concentration shows no great changes whether or not adding ZnCl_2 in the absence of catalyst. But, α -cellulose conversion is much affected by the content of ZnCl_2 . After adding 0.2 g ZnCl_2 , α -cellulose conversion is raised from 23.4% up to 44.1% (entry 6), glucose concentration decreases from 0.23 g L^{-1} to 0.15 g L^{-1} , while the productivity of LA, FA and 5-HMF are all increased. This indicates that ZnCl_2 can promote the hydrolysis of α -cellulose to glucose, which can be further transformed into 5-HMF. When only HZSM-5(25) catalyst is added, the conversion of α -cellulose is 63.9% at 200 °C after 2 h (entry 7) and 1.78 g L^{-1} of the overall product concentration toward glucose, levulinic acid and formic acid is obtained. Moreover, the FA and LA concentrations are up to 0.20 and 0.94 g L^{-1} and almost no 5-HMF is detected. These results suggested that HZSM-5 as active acid sites can promote quickly rehydrate of the yielding 5-HMF to FA and LA. It was shown that the conversion of α -cellulose and the total concentration of products first increase and then decrease with the increasing ZnCl_2 content when HZSM-5(25) and ZnCl_2 are added into the reactor together. Up to 84.2% of α -cellulose conversion and 5.23 g L^{-1} of total products concentration are obtained when 0.2 g ZnCl_2 and 0.4 g HZSM-5 are added (entry 8). However, when the content of ZnCl_2 is higher than 0.4 g, lower α -cellulose conversion (11.5%) and total products concentration (0.38 g L^{-1}) are obtained (entry 10). This indicates that a small amount of ZnCl_2 is effective in promoting the hydrolysis of α -cellulose. It is supposed that appropriate amount of ZnCl_2 is necessary for the cooperative or synergetic action of ZnCl_2 and HZSM-5. Too much ZnCl_2 may decrease the hydrolysis activity of HZSM-5 catalyst.

3.2.4. Effect of ultrasonic (US) pretreatment on α -cellulose hydrolysis

The influence of ultrasonic time over HZSM-5(25) is investigated and the results are shown in Fig. 6. It can be seen that α -cellulose conversion always keeps at about 23.3% with different ultrasonic time without catalyst (Fig. 6). Glucose concentration is increased from 0.23 to 0.84 g L^{-1} after ultrasonic treatment for 1 h in the absence of catalyst, but still no LA and FA are detected. By comparing the two blank reactions, the result indicates that ultrasonic pretreatment is favorable for the formation of glucose, while there is no significant increase in glucose yield with further prolonging ultrasonic time to 2 h. This indicates that glucose concentration is affected strongly by ultrasonic time and ultrasonic treatment has no obvious effect on LA and FA formation without catalyst. Under the similar reaction conditions, α -cellulose conversion is about 53.9% after adding 0.4 g HZSM-5(25) before ultrasonic treatment and this value is further increased to 63.9% after ultrasonic treatment for



Scheme 1. Reaction pathways for α -cellulose conversion in water over HZSM-5 catalysts.

2 h as shown in Fig. 6. The conversion of α -cellulose decreases to 59.0% and 50.9% after prolonging ultrasonic time to 3 h and 4 h, respectively. The results show the optimum ultrasonic time for α -cellulose hydrolysis is 2 h and the combined product concentration to glucose, 5-HMF, FA and LA is up to 1.63 g L^{-1} over HZSM-5(25) catalyst. The concentrations to glucose and 5-HMF are kept at about 0.2 and 0.02 g L^{-1} , respectively, with the increase of α -cellulose conversion. But, FA and LA concentrations increase sharply with α -cellulose conversion, implying that 5-HMF is further rehydrated to FA and LA on HZSM-5(25).

In order to gain more insight into the controlling factors on α -cellulose hydrolysis, the effect of the ultrasonic treatment and the degree of crystallinity of α -cellulose on hydrolysis of α -cellulose are further analyzed. It can be seen from Fig. 4, the ICR for α -cellulose, after 0, 1 and 2 h of ultrasonic pretreatment are 0.651, 0.615 and 0.564, respectively. It is found that there exists a good linear relationship between ICR value of α -cellulose and its conversion, indicating that ultrasonic treatment with appropriate time is an efficient method for decreasing crystallinity of α -cellulose and improving its hydrolysis.

3.3. Cellulose hydrolysis pathway

As discussed above, it can be seen that the catalytic hydrolysis of α -cellulose in aqueous-phase is a complex process, including breakage of β -1,4-glycosidic bond, isomerization, dehydration and hydration steps. Moreover, in this study the role of different types of acid sites on zeolite catalysts in this reaction has been investigated, including Brønsted or Lewis acid sites. From the experimental results, the possible reaction pathway of hydrolysis of α -cellulose in aqueous phase is proposed in Scheme 1. It can be seen that glucose is produced from α -cellulose firstly with the promotion of ultrasonic assisted and the external Brønsted acid sites of zeolite and then they are further transformed to 5-HMF. Generally, the conversion of glucose to 5-HMF would undergo two successive steps: isomerization to fructose by Lewis acid sites of HZSM-5 catalyst and then dehydration of fructose to 5-HMF over Brønsted acid sites of HZSM-5 [46], which indicates that glucose is the reaction intermediates for α -cellulose conversion to 5-HMF (see Supporting information, Table S2). When no catalyst is added, a 0.40 g L^{-1} of 5-HMF concentration with 23.4% of α -cellulose conversion can be obtained. Only a poor 5-HMF yield of 0.02 g L^{-1} with above 63.9% of cellulose conversion are obtained using HZSM-5 catalyst. This results confirm that both Lewis and Brønsted acid sites on the HZSM-5 catalyst are active enough to synergistically convert generated glucose to 5-HMF. Meanwhile, the HZSM-5 catalyst plays an important role

in the degradation of 5-HMF to LA and FA. Hence, the proposed reaction network of α -cellulose conversion to LA and FA over the HZSM-5 catalyst, as shown in Scheme 1, includes three steps: (1) α -cellulose is hydrolyzed into glucose at acid sites located on the outer surface of zeolite; (2) isomerization of glucose to fructose over Lewis acid sites and fructose further dehydration to 5-HMF by Brønsted acid sites; (3) the generated 5-HMF diffuses into micropores of HZSM-5 and hydrates to FA and LA on the inner surface of zeolite. All of the above results demonstrate that generated 5-HMF is consumed within 1 h and is almost fully converted to LA and FA over the HZSM-5 catalyst due to its poor stability in the water phase.

4. Conclusion

Liquid-phase hydrolysis of α -cellulose to glucose and other value-added products such as 5-HMF, levulinic acid (LA) and formic acid (FA) is carried out over HZSM-5 zeolites with different Si/Al ratio and pore structure. Low Si/Al ratio is beneficial to conversion of α -cellulose and the highest α -cellulose conversion (63.9%) and glucose (0.64 g L^{-1}) and LA (0.94 g L^{-1}) concentrations are obtained over HZSM-5(25). The parent HZSM-5(25) is dealuminated or desilicated using HCl or NaOH solution, respectively. The total amount of acid sites in desilicated HZSM-5 zeolite decrease slightly, but a remarkable decrease for dealuminated HZSM-5 zeolite compared to that of the parent HZSM-5. These modified HZSM-5 catalysts are applied to the hydrolysis of α -cellulose in a batch reactor. Compared to parent HZSM-5 catalysts, both dealuminated and desilicated HZSM-5 samples show a higher α -cellulose conversion. But the desilicated HZSM-5 with mesopores exhibits a much higher 5-HMF yield due to the conversion of large amount of intermediate glucose on the external acid sites of zeolite. It is found that ultrasonic pretreatment can reduce the crystallinity of α -cellulose and improve its dispersion in the water as well as the activity of α -cellulose hydrolysis. A marked improvement in α -cellulose conversion and LA or FA yields are obtained after suitable amounts of ZnCl₂ (0.2 g) and HZSM-5(25) are added together under ultrasonic treatment.

Acknowledgements

The authors would like to acknowledge the financial support from the National Natural Science Foundation of China (21433001, 21406251, 21403265, and 31470609), 13th Five-Year the National key R&D projects (2017YFD0600805), and The Young Taishan Scholars Program of Shandong Province (tsqn20161052).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.mcat.2017.11.032>.

References

- [1] G.W. Huber, R.D. Crighton, J.A. Dumesic, Renewable alkanes by aqueous-phase reforming of biomass-derived oxygenates, *Angew. Chem. Int. Ed.* 43 (2004) 1549–1551.
- [2] G.W. Huber, S. Iborra, A. Corma, *Chem. Rev.* 106 (2006) 4044–4098.
- [3] Z. Xiao, S. Jin, M. Pang, C. Liang, Conversion of highly concentrated cellulose to 1,2-propanediol and ethylene glycol over highly efficient CuCr catalysts, *Green Chem.* 15 (2013) 891–895.
- [4] 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 H-ZSM-5 catalyst, *Acs Sustain. Chem. Eng.* 2 (2014) 1928–1932.
- [5] W. Deng, Q. Zhang, Y. Wang, Catalytic transformations of cellulose and its derived carbohydrates into 5-hydroxymethylfurfural levulinic acid, and lactic acid, *Sci. China Chem.* 58 (2015) 29–46.
- [6] L.C. Duarte, T. Silva-Fernandes, F. Carvalheiro, F.M. Gírio, *Appl. Biochem. Biotechnol.* 153 (2009) 116.
- [7] R. Rinaldi, R. Palkovits, F. Schüth, Depolymerization of cellulose using solid catalysts in ionic liquids, *Angew. Chem. Int. Ed.* 47 (2008) 8047–8050.
- [8] M. Cheng, T. Shi, H. Guan, S. Wang, X. Wang, Z. Jiang, Clean production of glucose from polysaccharides using a micellar heteropolyacid as a heterogeneous catalyst, *Appl. Catal. B Environ.* 107 (2011) 104–109.
- [9] R. Kourieh, S. Bennici, M. Marzo, A. Gervasini, A. Auroux, Investigation of the WO_3/ZrO_2 surface acidic properties for the aqueous hydrolysis of cellobiose, *Catal. Commun.* 19 (2012) 119–126.
- [10] Z. Fang, F. Zhang, H.Y. Zeng, F. Guo, Production of glucose by hydrolysis of cellulose at 423 K in the presence of activated hydrotalcite nanoparticles, *Bioresour. Technol.* 102 (2011) 8017–8021.
- [11] H. Kobayashi, T. Komano, K. Hara, A. Fukuoka, Water-tolerant mesoporous-carbon-supported ruthenium catalysts for the hydrolysis of cellulose to glucose, *ChemSusChem* 3 (2010) 440–443.
- [12] H. Guo, X. Qi, L. Li S.R. Jr, Hydrolysis of cellulose over functionalized glucose-derived carbon catalyst in ionic liquid, *Bioresour. Technol.* 116 (2012) 355–359.
- [13] I. Aguirrezaabal-Telleria, I. Gandarias, P.L. Arias, Heterogeneous acid-catalysts for the production of furan-derived compounds (furfural and hydroxymethylfurfural) from renewable carbohydrates: a review, *Catal. Today* 234 (2014) 42–58.
- [14] L.H. Chen, X.Y. Li, J.C. Rooke, Y.H. Zhang, X.Y. Yang, Y. Tang, F.S. Xiao, B.L. Su, *J. Mater. Chem. A* 22 (2012) 17381.
- [15] C.W. Jiang, X. Zhong, Z.H. Luo, *RSC Adv.* 4 (2014) 15216.
- [16] P. Lanzafame, D.M. Temi, S. Perathoner, A.N. Spadaro, G. Centi, Direct conversion of cellulose to glucose and valuable intermediates in mild reaction conditions over solid acid catalysts, *Catal. Today* 179 (2012) 178–184.
- [17] A. Onda, T. Ochi, K. Yanagisawa, Selective hydrolysis of cellulose into glucose over solid acid catalysts, *Green Chem.* 10 (2008) 1033–1037.
- [18] Z. Zhang, Z.K. Zhao, Solid acid and microwave-assisted hydrolysis of cellulose in ionic liquid, *Carbohydr. Res.* 344 (2009) 2069–2072.
- [19] H. Cai, C. Li, A. Wang, G. Xu, T. Zhang, Zeolite-promoted hydrolysis of cellulose in ionic liquid, insight into the mutual behavior of zeolite, cellulose and ionic liquid, *Appl. Catal. B Environ.* 123–124 (2012) 333–338.
- [20] P. Daorattanachai, S. Namuangruk, N. Viriya-empikul, N. Laosiripojana, K. Faungnawakij, 5-Hydroxymethylfurfural production from sugars and cellulose in acid- and base-catalyzed conditions under hot compressed water, *J. Ind. Eng. Chem.* 18 (2012) 1893–1901.
- [21] H.F. Lin, J. Strull, Y. Liu, Z. Karmiol, K. Plank, G. Miller, Z.H. Guo, L.S. Yang, High yield production of levulinic acid by catalytic partial oxidation of cellulose in aqueous media, *Energy Environ. Sci.* 5 (2012) 9773–9777.
- [22] L. Zhou, M. Shi, Q. Cai, L. Wu, X. Hu, X. Yang, C. Chen, J. Xu, Hydrolysis of hemicellulose catalyzed by hierarchical H-USY zeolites – the role of acidity and pore structure, *Microporous Mesoporous Mat.* 169 (2013) 54–59.
- [23] A. Fukuoka, P.L. Dhepe, Catalytic conversion of cellulose into sugar alcohols, *Angew. Chem. Int. Ed.* 45 (2006) 5161–5163.
- [24] N. Ji, T. Zhang, M.Y. Zheng, A.Q. Wang, H. Wang, X.D. Wang, J.G.G. Chen, Direct catalytic conversion of cellulose into ethylene glycol using nickel-promoted tungsten carbide catalysts, *Angew. Chem. Int. Ed.* 47 (2008) 8510–8513.
- [25] Y. Habibi, I. Hoeger, S.S. Kelley, O.J. Rojas, Development of Langmuir-Schaeffer cellulose nanocrystal monolayers and their interfacial behaviors, *Langmuir* 26 (2010) 990–1001.
- [26] L. Segal, J.J. Creely, A.E. Martin, C.M. Conrad, An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer, *Text. Res. J.* 29 (1959) 786–794.
- [27] W. Deng, X. Tan, W. Fang, Q. Zhang, Y. Wang, Conversion of cellulose into sorbitol over carbon nanotube-supported ruthenium catalyst, *Catal. Lett.* 133 (2009) 167–174.
- [28] M.A. Camblor, A. Corma, S. Valencia, Spontaneous nucleation and growth of pure silica zeolite-beta of connectivity defects, *Chem. Commun.* 20 (1996) 2365–2366.
- [29] L. Rodríguez-González, F. Hermes, M. Bertmer, E. Rodríguez-Castellón, A. Jiménez-López, U. Simon, The acid properties of H-ZSM-5 as studied by NH_3 – TPD and ^{27}Al -MAS-NMR spectroscopy, *Appl. Catal. A* 328 (2007) 174–182.
- [30] C.V. Hidalgo, H. Itoh, T. Hattori, M. Niwa, Y. Murakami, Measurement of the acidity of various zeolites by temperature-programmed desorption of ammonia, *J. Catal.* 85 (1984) 362–369.
- [31] G. Tonetto, J. Atias, H. de Lasa, FCC catalysts with different zeolite crystallite sizes: acidity, structural properties and reactivity, *Appl. Catal. A* 270 (2004) 9–25.
- [32] L. Zhou, Z. Liu, Y. Bai, T. Lu, X. Yang, J. Xu, Hydrolysis of cellobiose catalyzed by zeolites—the role of acidity and micropore structure, *J. Energy Chem.* 25 (2016) 141–145.
- [33] S.M. Opalka, T. Zhu, Influence of the Si/Al ratio and Al distribution on the H-ZSM-5 lattice and brønsted acid site characteristics, *Microporous Mesoporous Mater.* 222 (2015) 256–270.
- [34] P. Kalita, N.M. Gupta, R. Kumar, Synergistic role of acid sites in the Ce-enhanced activity of mesoporous Ce-Al-MCM-41 catalysts in alkylation reactions: FTIR and TPD-ammonia studies, *J. Catal.* 245 (2007) 338–347.
- [35] N. Liu, X. Pu, X. Wang, L. Shi, Study of alkylation on a lewis and brønsted acid hybrid catalyst and its industrial test, *J. Ind. Eng. Chem.* 20 (2014) 2848–2857.
- [36] T. Armaroli, L.J. Simon, M. Digne, T. Montanari, M. Bevilacqua, V. Valtchev, J. Patarin, G. Busca, Effects of crystal size and Si/Al ratio on the surface properties of H-ZSM-5 zeolites, *Appl. Catal. A* 306 (2006) 78–84.
- [37] L. Shirazi, E. Jamshidi, M.R. Ghasemi, The effect of Si/Al ratio of ZSM-5 zeolite on its morphology, acidity and crystal size, *Cryst. Res. Technol.* 43 (2008) 1300–1306.
- [38] M.E. Himmel, S.Y. Ding, D.K. Johnson, W.S. Adney, M.R. Nimlos, J.W. Brady, T.D. Foust, Biomass recalcitrance: engineering plants and enzymes for biofuels production, *Science* 315 (2007) 804–807.
- [39] P.P. Zhang, D.S. Tong, C.X. Lin, H.M. Yang, Z.K. Zhong, H. Wang, C.H. Zhou, Effects of acid treatments on bamboo cellulose nanocrystals, *Asia-Pac. J. Chem. Eng.* 9 (2014) 686–695.
- [40] K. Shimizu, H. Furukawa, N. Kobayashi, Y. Itaya, A. Satsumi, Effects of Brønsted and Lewis acidities on activity and selectivity of heteropolyacid-based catalysts for hydrolysis of cellobiose and cellulose, *Green Chem.* 11 (2009) 1627–1632.
- [41] L. Zhou, Z. Liu, M. Shi, S. Du, Y. Su, X. Yang, J. Xu, Sulfonated hierarchical H-USY zeolite for efficient hydrolysis of hemicellulose/cellulose, *Carbohydr. Polym.* 98 (2013) 146–151.
- [42] R. Srivastava, M. Choi, R. Ryoo, Mesoporous materials with zeolite framework: remarkable effect of the hierarchical structure for retardation of catalyst deactivation, *Chem. Commun.* 43 (2006) 4489–4491.
- [43] K. Suzuki, Y. Aoyagi, N. Katada, M. Choi, R. Ryoo, M. Niwa, Acidity and catalytic activity of mesoporous ZSM-5 in comparison with zeolite ZSM-5, Al-MCM-41 and silica-alumina, *Catal. Today* 132 (2008) 38–45.
- [44] R. Rinaldi, F. Schüth, Design of solid catalysts for the conversion of biomass, *Energy Environ. Sci.* 2 (2009) 610–626.
- [45] H. Wang, L. Zhang, D. Tian, R. Hao, X. Hou, J.R. Cort, B. Yang, ZnCl_2 induced catalytic conversion of softwood lignin to aromatics and hydrocarbons, *Green Chem.* 18 (2016) 2802–2810.
- [46] S. Van de Vyver, J. Geboers, M. Dusselier, H. Schepers, T. Vosch, L.A. Zhang, G. Van Tendeloo, P.A. Jacobs, B.F. Sels, Selective bifunctional catalytic conversion of cellulose over reshaped Ni particles at the tip of carbon nanofibers, *ChemSusChem* 3 (2010) 698–701.