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

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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, $ZnCl_2$ 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 $ZnCl_2$ 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.

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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, Hβ, 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 Hβ 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 $[C_4mim]Cl$ as solvent under microwave irradiation [18]. In this context, Zhang and co-workers investigated a variety of H-type zeolites (HY, Hβ, 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

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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 magor 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, $ZnCl_2$ content and ultrasonic pretreatment on products distribution of α-cellulose hydrolysis are also demonstrated. By combination of XRD, physisorption, FT-IR, NH_3-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 NH_4NO_3 solution at 85 °C and washed with a large amount of deionized water, repeatedly. After drying, the samples in NH_4-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 product 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 Kα source (λ = 0.154 nm) in a 2θ 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. NH_3-temperature-programmed desorption (NH_3-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 μm 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:

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

Concentration changes of main products such as glucose, 5-HMF, LA and FA were quantitatived 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 H_2SO_4 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

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