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Hydrolysis of cellobiose catalyzed by zeolites—the role of acidity and micropore structure

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ABSTRACT

The roles of acidity and micropore structure of zeolite were studied in the hydrolysis of the model oligosaccharide of cellulose–cellobiose. HZSM-5, HY, HMOR and Hβ zeolites were selected as model catalysts for the hydrolysis of cellobiose. The effect of acidity of zeolite, including the strength, type and location, on its catalytic activity was investigated. The strong Brönsted acid sites located in micropores are the active sites for the hydrolysis of cellobiose to glucose. Meanwhile, the catalytic performance of zeolite is also dependent on the micropore size of zeolite.

1. Introduction

Depolymerization of cellulose to glucose is an important process and remains a challenge for the conversion of lignocellulosic biomass to fuels and chemicals [1]. Cleavage of the glycosidic bonds of cellulose is usually catalyzed by enzymes or acids. Enzymes can catalyze the hydrolysis of cellulose under mild conditions [2]. However, the need of pretreatment for raw materials, the low reaction rate, the high cost of enzyme, and the difficulty of recovering the enzyme from the reaction mixture are the main challenges [3]. Mineral acids have been studied for cellulose hydrolysis widely. However, the use of mineral acids is wasteful and energy-inefficient, requiring separation, recycling, and treatment of the acid waste residue [4]. For these reasons, heterogeneous solid catalysts would be favorable choices for cellulose hydrolysis to monomeric sugar. Various solid acids including sulfonated carbon [5,6], sulfonic acid resin [7], zeolites [8,9], and sulfonic acid-functionalized SiO_2 [10] have been studied to catalyze cellulose hydrolysis.

Among these solid acids, zeolite is one of the promising catalysts due to its crystalline structure, uniform pore size, high surface area, flexible framework, and tunable acidity [11]. Recently, our group reported that mesoporous HUSY zeolite efficiently catalyzed the hydrolysis of hemicelluloses [12]. It was found that meso/macropores and large external area benefited both the catalytic activity and the selectivity for monosaccharides. Mesoporous HUSY was obtained through the severe acid-dealumination method which greatly decreased the acidity of the catalyst. This is unfavorable for the hydrolysis of polysaccharides. Modification of surfaces with acid groups is an effective method to improve the acidity of solid materials [13]. Sulfonated mesoporous HUSY zeolite showed much higher activity for hydrolysis of hemicelluloses/cellulose than the parent HUSY and the mesoporous HUSY [14]. As known, the cellulose chains are 'bundled' together to form so called cellulose fibrils or cellulose bundles [15]. The size of cellulose bundles is too large to enter the micropores of zeolite. These cellulose fibrils do not dissolve in water and most of organic solvents. Due to the low solubility, hydrolysis of cellulose in water can only proceed at the external surface or in meso/macropore to give oligosaccharides in the first step. The formed soluble oligosaccharides with linear molecular structure, for example, cellobiose with molecular dimension (MD) of 0.50 nm × 0.57 nm × 1.0 nm, could diffuse into the micropores of zeolite [16]. Oligosaccharides will be further hydrolyzed to monosaccharides catalyzed by the acid sites in the micropores. The contribution of the meso/macropore and the external surface area to the catalytic hydrolysis of biomass has been studied widely [8,12,14]. However, the effects of the acidity and micropore structure of zeolite on the hydrolysis of oligosaccharides from cellulose to monosaccharides in water are not very clear till now.

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Table 1. The physical parameters of zeolites.

Sample	$n_{(Si)}/n_{(Al)}$[a]	D_p (Å)[b]	Average D_p (Å)[c]	S_{BET} (m^2/g)[d]	S_{ex} (m^2/g)[d]	V_{total} (mL/g)[d]	V_{meso} (mL/g)[d]
HY	2.55	7.4 × 7.4	7.4	632	92	0.40	0.10
HMOR	12.97	6.5 × 7.0	6.75	448	105	0.32	0.14
HZSM-5	28.31	5.3 × 5.6, 5.1 × 5.1	5.45	274	~0	0.14	~0
Hβ	38.11	6.6 × 6.7, 5.5 × 5.6	6.65	495	72	0.33	0.09

[a] $n_{(Si)}/n_{(Al)}$ is the mole ratio of Si to Al of the zeolite.
[b] D_p represents the micropore diameter from reference [15].
[c] Average pore diameter is the mean value of the size of large pore in two dimensions.
[d] S_{BET}, V_{total}, S_{ex} and V_{meso} are the total surface area, total pore volume, external surface area and mesopore volume, respectively.

The present work aims to investigate the behaviors of acidity and micropore structure of zeolites in the hydrolysis of model disaccharide-cellobiose. Zeolites including HY, Hβ, HZSM-5 and HMOR were selected as model catalysts. This study will be helpful for developing efficient solid catalysts for biomass conversion.

2. Experimental

2.1. Materials

Commercially available Na-type zeolites were purchased from Nankai University Catalyst Co. (China). NH_4-type zeolites were obtained by ion-exchanging twice with 0.5 M NH_4NO_3 solution (liquid/solid = 10 mL/g) at 80 °C for 2 h. The protonic form was obtained by calcination of the NH_4-type zeolites at 550 °C for 5 h. XRD patterns of HY, HMOR, HZSM-5 and Hβ showed that these zeolites were in the corresponding pure phase (Fig. S1). N_2 adsorption and desorption isotherms of these samples exhibited a typical isotherm of microporous materials (Fig. S2). Cellobiose (98%) was purchased from Alfa Aesar (China) Chemical Co., Ltd. The other reagents were of analytic grade and obtained from the commercial sources without further purification.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) was performed on a Panalytical X'pert PRO instrument with Cu $K\alpha$ (λ = 0.15418 nm) radiation. The chemical composition of zeolites was analyzed by a Philips Margix X-ray fluorescence (XRF) spectrometer. The adsorption/desorption isotherms were measured with a Quantachrome Autosorb using N_2 as adsorbate at −196 °C. Samples were outgassed at 300 °C for 2 h prior to measurements. Total surface area was calculated according to the BET method, and mesopore diameters were calculated from the desorption branch of the isotherm based on the BJH method. The textural parameters determined by N_2 adsorption–desorption are shown in Table 1.

Acidities of the samples were characterized by temperature-programmed desorption of ammonia (NH_3-TPD) on a Micromeritics AutoChem II 2920 instrument. Before the adsorption of NH_3, the sample (~0.1 g) was pretreated at 350 °C in He (30 mL/min) for 30 min. Then the sample was cooled down to 100 °C and adsorbed NH_3 for 0.5 min. Subsequently, the catalyst was flushed with He until the baseline was steady. The desorption process was monitored with a thermal conductivity detector at a temperature ramp from 100 to 800 °C, with a heating rate of 10 °C/min.

Meanwhile, the Brönsted and Lewis acid sites of the catalysts were determined by Fourier Transform Infrared (FT-IR) spectroscopy with pyridine as a probe molecule. The spectra were recorded using Nicolet IR 200 FT-IR spectrometer at 150 °C with a resolution of 4 cm^{-1} on self-supporting pellets.

2.3. Studies of catalytic activity

Hydrolysis of cellobiose was performed in a 10 mL Teflon lined stainless steel autoclave reactor. After addition of desired amount of reactants and catalyst in water (5 mL), the autoclave was sealed. The atmosphere over the mixture was replaced four times with N_2. Subsequently, the reactor was heated to the desired temperature with stirring. When the reaction was finished, the reactor was cooled down to the ambient temperature. The reaction mixture was separated to liquid and solid phases by centrifugation and decantation. Analysis of the liquid samples was performed on a Shimadzu LC-20A equipped with a degasser DGU-20A3, a pump system (LC-20AT), an oven CTO-20AC maintained at 40 °C, an Aminex HPX-87H (Bio-Rad) HPLC column, and a refractive index detector. The mobile phase was 5 mM H_2SO_4 with a flow rate of 0.6 mL/min.

3. Results and discussion

3.1. The results for cellobiose hydrolysis

Table 2 shows the results of cellobiose hydrolysis over different catalysts. The main product is glucose with 5-hydroymethyl furfural (HMF) and its derivatives as by-products which are identified by GC-MS. In blank experiment, 20% of cellobiose was hydrolyzed with 96% selectivity to glucose (Table 2, entry 1). When HY, HMOR, HZSM-5 and Hβ were used as catalysts, 24%, 56%, 65% and 69% yields of glucose were obtained, respectively (Table 2, entries 2–5).

Hβ showed the best catalytic performance with 76% conversion of cellobiose and 91% selectivity to glucose (Table 2, entry 5). When the reaction temperature was elevated to 175 °C, 82% conversion of cellobiose with 92% selectivity to glucose could be obtained at the reaction time of 1 h (Table 2, entry 6). These results indicate that zeolites can effectively catalyze the hydrolysis of cellobiose. The activity

Table 2. Hydrolysis of cellobiose catalyzed by zeolites.

Entry	Catalyst	Conversion (%)	Glucose yield (%)	Glucose selectivity (%)	HMF selectivity (%)	TOF (h^{-1})[a]
1	Blank	20	19	96	4	–
2	HY	39	24	61	10	0.053
3	HMOR	60	56	94	4	0.156
4	HZSM-5	71	65	91	~0	0.146
5	Hβ	76	69	91	~0	0.250
6	Hβ[b]	82	75	92	~0	0.270

Reaction conditions: cellobiose (50 mg), catalyst (50 mg), water (5 mL), N_2 (1.0 MPa), 150 °C, 6 h.
[a] TOF value was calculated based on the acidity sites.
[b] 175 °C, 1 h.