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Sulfonated hierarchical H-USY zeolite for efficient hydrolysis of hemicellulose/cellulose

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ABSTRACT

Sulfonated hierarchical H-USY zeolite was prepared and characterized by X-ray diffraction, N_2 physisorption, Fourier transform infrared spectroscopy, inductively coupled plasma atomic emission spectroscopy, temperature-programmed desorption of ammonia, and acid–base titration. It was proved that sulfonic group was successfully anchored onto the hierarchical H-USY zeolite. The acidity of the hierarchical H-USY was remarkably improved. Sulfonated hierarchical H-USY zeolite was efficient for the hydrolysis of hemicellulose and cellulose. The yield of TRS for hydrolysis of hemicellulose reached 78.0% at 140 °C for 9 h. For hydrolysis of α-cellulose, 60.8% conversion with 22.4% yield of glucose was obtained. Even for microcrystalline cellulose, 43.7% conversion with 15.1% yield of glucose can be obtained. These results are much higher than those obtained over hierarchical H-USY zeolite, indicating that both the acidity and the pore structure determine the activity of zeolite as catalyst in the hydrolysis of biomass.

1. Introduction

With the gradual consumption of fossil resources, utilization of renewable resources to complement or replace fossil resources has attracted more and more attention (Perego & Bosetti, 2011). Abundant and sustainable plant biomass is one of the main alternative resources. However, the efficient utilization of hemicellulose and cellulose, which are the major components of plant biomass and account for 60–90 wt.% of plant biomass (Alonso, Bond, & Dumesic, 2010; Liu & Chen, 2012), is yet an intractable problem. Sugars produced from the hydrolysis of hemicellulose and cellulose are the key platform molecules of biomass transformation processes, which can be further converted to biofuels and other high-value added chemicals (De et al., 2012; Stöker, 2008). Consequently, hydrolysis of hemicellulose and cellulose to sugars is one of the important research domains of biomass utilization currently (Sasaki, Sumimoto, Asada, & Nakamura, 2012).

Both hemicellulose and cellulose are polysaccharides formed by the linkage of monosaccharides via glycosidic bonds. Hemicellulose is heteropolysaccharide, generally comprised of five different sugar monomers (D-xylose, L-arabinose, D-galactose, D-mannose, and D-glucose), with xylose being the most abundant (Dhepe & Sahu, 2011). Cellulose is homopolysaccharide, consisting of D-glucose linked by 1,4-β-glycosidic bonds to form linear polymeric chains. Hydrolysis of glycosidic bonds of hemicellulose and cellulose can be catalyzed by either enzymes or acids. Usually, acid hydrolysis is considered to be more efficient than the enzymatic hydrolysis (Duarte, Silva-Fernandes, Carvalheiro, & Gírio, 2009). Traditionally, mineral acids, such as HCl and H_2SO_4, are used to hydrolyze hemicellulose and cellulose, but their use is wasteful and energy-inefficient, requiring separation, recycling, and treatment of the acid waste residue. Therefore, various solid acid catalysts, including zeolite materials (Zhang & Zhao, 2009), sulfonated carbon (Guo, Qi, Li, & Smith, 2012), sulfonated resins (Rinaldi, Palkovits, & Schüth, 2008), heteropolyacid (Cheng et al., 2011), sulfonic acid functionalized silica (Amarasekara & Owereh, 2010), WO_3/ZrO_2 (Kourieh, Bennici, Marzo, Gervasini, & Auroux, 2012), hydrotalcite (Fang, Zhang, Zeng, & Guo, 2011), and Ru/CMK (Kobayashi, Komanoya, Hara, & Fukuoka, 2010), were developed to hydrolyze hemicellulose and/or cellulose to sugars in recent years.

When solid catalysts and environmentally friendly water as solvent are used, the hydrolysis of hemicellulose/cellulose can only proceed at the interface of solid catalyst and hemicellulose/cellulose due to the low solubility of hemicellulose and cellulose in water. So, large pore diameter and high external area are favorable for the hydrolysis of biomass using solid materials as catalysts. Very recently, our group reported hierarchical H-USY zeolite (H-USY-meso) with meso/micropores and large external

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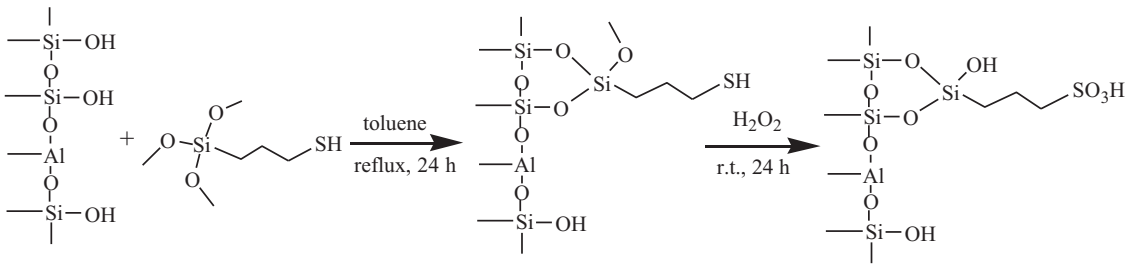

Scheme 1. The synthesis route of H-USY-meso-SO_3H.

area for the hydrolysis of hemicelluloses (Zhou et al., 2013). 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. In view of acid-catalyzed hydrolysis of polysaccharides, high acid strength and large amount of acid sites are helpful for increasing the activity of catalyst, especially for hydrolysis of recalcitrant cellulose. Therefore, sulfonated hierarchical H-USY zeolite (H-USY-meso-SO_3H) was prepared to increase the acidity of catalyst in present work. It was found that H-USY-meso-SO_3H showed much higher activity for hydrolysis of hemicellulose and cellulose than H-USY and H-USY-meso.

2. Methods

2.1. Materials

H-USY powder (Si/Al = 3.2) was purchased from Nankai University Catalyst Co. (China). Oxalic acid (AR, 99.8%) was purchased from Tianjin No. 3 Chemical Reagent Factory. Dry toluene was obtained by distillation of toluene (AR) in the presence of metallic sodium. 3-Mercaptopropyltrimethoxysilane (AR) was purchased from Aladdin-reagent Co. (China). Hardwood (Beechwood, xylose > 90%) derived hemicelluloses (xylan) and α-cellulose were purchased from Sigma–Aldrich. Microcrystalline cellulose (MCC) was purchased from Alfa Aesar.

2.2. Preparation and characterization of H-USY-meso-SO_3H

Firstly, H-USY-meso was prepared by oxalic acid leaching method. H-USY (4.0 g) and 100 mL of aqueous solution of oxalic acid (the concentration is 0.2 mol L^{-1}, unless otherwise noted) were added in a three-necked flask equipped with a reflux condenser. After treatment at 85 °C for 8 h under stirring, the sample was filtered, washed with deionized water, dried at 120 °C for 12 h, and calcined at 550 °C for 5 h.

Scheme 1 summarizes the synthesis route for H-USY-meso-SO_3H. In a typical synthesis, the obtained H-USY-meso (2 g) was added into dry toluene (40 mL). After reflux at 110 °C for 1 h under nitrogen atmosphere with stirring, 1.57 g of 3-mercaptopropyltrimethoxysilane was added. The mixture further refluxed for 24 h. The final product was filtered, washed with ethanol for several times, and dried overnight at 60 °C. Subsequently, 1 g of the product was added into 60 mL of H_2O_2 (30%, w/v), and the mixture was stirred at room temperature for 24 h. The solid was filtered and washed with deionized water for three times. Finally, the obtained material was dried overnight at 100 °C. For comparison, H-USY was also sulfonated using same procedure which was denoted as H-USY-SO_3H.

Powder X-ray diffraction (XRD) was performed on a Panalytical X'pert PRO instrument with Cu Kα (λ = 0.15418 nm) radiation. The adsorption/desorption isotherms were measured with a Quantachrome Autosorb using N_2 as adsorbate at −196 °C. Samples were outgassed at 150 °C for 1.5 h prior to measurements. Total surface area was calculated according to Barrett–Emmet–Taller (BET) method, and pore size distributions were calculated from the desorption branch of the isotherm based on Barrett–Joyner–Halenda (BJH) method. Fourier transform infrared spectroscopy was recorded using a Nicolet IR 200 Spectrometer in KBr media. Sulfur content was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a TJA Advantage ICP-AES instrument.

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^{-1}) 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^{-1}.

The acid density was estimated by exchange of protons with Na^+ in aqueous NaCl. Sample was dispersed in NaCl solution (2 mol L^{-1}), and then the above mixture was stirred at room temperature for 12 h. After the sample was filtrated, the acid amount in the solution was measured by titration with NaOH (5 mmol L^{-1}).

2.3. Hydrolysis of hemicellulose and cellulose

Hydrolysis of hemicellulose or cellulose was performed in a 100 mL Teflon-lined stainless steel autoclave reactor. After addition of desired amount of reactants and catalysts in water (30 mL), the autoclave was sealed. The atmosphere over the mixture was replaced with N_2 for four times. Subsequently, the reactor was heated to the desired temperature with stirring, and the pressure of N_2 was charged to 1.0 MPa. When the reaction finished, the reactor was cooled down to the ambient temperature. The reaction mixture was separated to liquid and solid phases by centrifugation and decantation. The total reducing sugars (TRS) in the aqueous solution were analyzed using an established method with 3,5-dinitrosalicylic acid (DNS method) (Jiang, Ma, & Bao, 2009). The mixture of DNS reagent (0.5 mL) and the dilute reaction solution (0.5 mL) was heated for 20 min at 100 °C, then cooled down to room temperature quickly, and diluted to 5 mL. The absorbance of the dilute solution was measured on a 721 spectrophotometer (Shanghai, China) at 511 nm. The amount of TRS was calculated using a standard curve prepared using xylose or glucose for hemicellulose and cellulose, respectively.

The mass of TRS (M_{TRS}) and the yield of TRS were calculated as follows:

$$M_{TRS} = N \times V \times C \quad (1)$$

$$\text{Yield}_{TRS}\ (\%) = \frac{0.88 \times M_{TRS}}{W} \times 100 \quad (2)$$

$$\text{Yield}_{\text{TRS}}\ (\%) = \frac{0.90 \times M_{\text{TRS}}}{W} \times 100 \quad (3)$$

where M_{TRS} is the mass of TRS in reaction solution, N is the multiple for diluting the reaction solution, V is the volume of the reaction solution, C is the concentration of TRS calculated from the standard curve, and W is the mass of hemicellulose or cellulose initially loaded for the reaction, respectively. For the hemicellulose and cellulose, the yield of TRS was calculated by formula (1), (2) and (1), (3), respectively.

The glucose concentration in the reaction solution was analyzed by an SBA-50B glucose analyzer (Shandong Academy of Sciences, Jinan, China), and its yield was calculated using the following formula:

$$M_{\text{glucose}} = N \times V \times C$$

$$\text{Yield}_{\text{glucose}}\ (\%) = \frac{0.90 \times M_{\text{glucose}}}{W} \times 100$$

where M_{glucose} is the mass of glucose in reaction solution, N is the multiple for diluting the reaction solution, V is the volume of the reaction solution, C is the concentration of glucose measured by glucose analyzer, and W is the mass of cellulose initially loaded for the reaction.

3. Results and discussion

3.1. Preparation and characterization of H-USY-meso-SO_3H

Oxalic acid, as an acid and a chelating agent for metal ion, is effective for the extraction of aluminum from aluminosilicate zeolite. Therefore, H-USY was treated with oxalic acid to extract aluminum and generate meso/macropores. H-USY-meso, prepared by oxalic acid treatment of H-USY, have plenty of meso/macropores and large external surface area. The meso/macropores in zeolites are helpful for the diffusion of reactant and products (Zhou et al., 2012). So, H-USY-meso showed good activity for hydrolysis of hemicelluloses. However, the dealumination process for preparing hierarchical zeolites also led to the decrease of acidity. For example, the acid amount decreased about 90% after H-USY was treated by oxalic acid (0.2 mol L^{-1}) at 85 °C for 8 h (Zhou et al., 2013). In view of the acid-catalyzed hydrolysis of hemicellulose and cellulose, it is necessary to improve the acidity of H-USY-meso to obtain a catalyst with excellent performance. The surface of H-USY-meso has abundant hydroxyls as proved by NH_3-TPD experiment and FT-IR, which makes it possible to anchor sulfonic group onto H-USY-meso. Here, H-USY-meso-SO_3H was synthesized by the post-grafting method.

From XRD patterns of H-USY, H-USY-SO_3H, H-USY-meso and H-USY-meso-SO_3H (Fig. S1, Supplementary material), it can be seen that the position of diffraction peaks of these materials is similar and no new diffraction peaks appear. However, the intensity of diffraction peaks of H-USY-meso-SO_3H is lower than H-USY-meso. At the same time, the diffraction peaks of H-USY-SO_3H are also weaker than those of H-USY. The decrease of the intensity of diffraction peaks is caused by the modified groups. Similar result was reported for the sulfonic acid-functionalized SBA-15 (Liu et al., 2011).

Table 1 shows the physical properties of different samples. The surface area, total pore volume, external surface area and mesopore volume of H-USY-meso are larger than H-USY. After sulfonation, these parameters of H-USY-meso-SO_3H decrease, which is caused by the block effect of sulfonic groups (Liu et al., 2011). The external surface area and mesopore volume are still larger than H-USY. However, the surface area and pore volume of H-USY-SO_3H are much lower than H-USY, indicating that the pores are severely blocked by sulfonic groups.

The acidity was characterized by NH_3-TPD (Fig. S2, Supplementary material). Except for H-USY-meso, the other samples show two main peaks, corresponding to NH_3 desorbed from weak and strong acid sites (Ma et al., 2007), respectively. For H-USY-meso, the peak at the temperature higher than 400 °C belongs to the dehydration of plenty of Si–OH generated by acid treatment (Triantafillidis, Vlessidis, & Evmiridis, 2000). The acidity of H-USY-meso is much lower than H-USY, which is induced by dealumination through acid treatment to generate meso/macropores. Both the amount and the strength of acid sites of H-USY-meso-SO_3H increase remarkably after sulfonation. The peak at 462 °C is related to —SO_3H. The sulfur content of H-USY-meso-SO_3H determined by ICP-AES is 0.16 mmol g^{-1}. These data imply that —SO_3H groups are successfully immobilized on H-USY-meso zeolite. The intensity of the peak at 209 °C, corresponding to weak acid sites of H-USY-meso-SO_3H, is much stronger than that of H-USY-meso (150 °C). These acid sites may be formed by the condensation between the extraframework aluminum species and Si–OH in the reflux process in dry toluene. For comparison, functionalization of H-USY with sulfonic acid was also studied. It can be seen that the amount of both weak and strong acid sites of H-USY-SO_3H increases compared with H-USY. However, the increase of the intensity of weak acid sites is not obvious in comparison with H-USY-meso-SO_3H. The total acid density was determined by NaOH titration (Table 1). The acid density varied in the following order: H-USY-meso (0.09 mmol g^{-1}) < < H-USY (0.26 mmol g^{-1}) < H-USY-SO_3H (0.29 mmol g^{-1}) < H-USY-meso-SO_3H (0.40 mmol g^{-1}). This is accordant with the results of NH_3-TPD.

FT-IR spectra of H-USY-meso and H-USY-meso-SO_3H are presented in Fig. S3, Supplementary material. Although the vibration absorption bands of sulfonic acid group overlap with those of zeolite framework, there are still some difference between the spectra of H-USY-meso and H-USY-meso-SO_3H. In comparison with H-USY-meso, the spectrum of H-USY-meso-SO_3H shows a weak peak at 2934 cm^{-1} that is attributed to the asymmetric stretching vibration of CH_2 (Yang, Wei, Su, & Zhou, 2010). Moreover, the intensity of other two bands near 1170 cm^{-1} and 795 cm^{-1} increases after functionalization with sulfonic acid. The band at ~1170 cm^{-1} is assigned to the asymmetric and symmetric stretching of S=O bond, and the other band at ~795 cm^{-1} is attributed to the S—O bond (Kalbasi, Massah, & Shafiei, 2011). The results elucidate that sulfonic acid groups are successfully grafted onto the surface of hierarchical H-USY zeolite.

3.2. Catalytic performance of sulfonated hierarchical H-USY zeolites

3.2.1. Hydrolysis of hemicellulose

The hydrolysis of hemicellulose (xylan) was studied using different type zeolites as catalysts to obtain the relationship between the pore structure, acidity and the catalytic performance of zeolites (Fig. 1). Among these catalysts, H-USY-meso-SO_3H with both strong acidity and meso/macropores gives the highest TRS yield of 78% at 140 °C for 9 h. At the same reaction conditions, H-USY-SO_3H with only strong acidity shows the TRS yield of 28%. For H-USY-meso with only abundant meso/macropores, 35% of TRS yield is obtained. The lowest TRS yield of 19% is obtained over H-USY with neither strong acid sites nor meso/macropores. From above results, it can be concluded that strong acidity and large amount of meso/macropores are the two key factors for solid catalyst to achieve high TRS yield in hydrolysis of hemicellulose.

Since H-USY-meso-SO_3H shows good catalytic performance for hydrolysis of hemicelluloses, it was chosen for more detailed studies. Fig. 2a displays the reaction temperature on the hydrolysis of hemicellulose (xylan). The yield of TRS increases from 24% to 76% as the reaction temperature was elevated from 130 °C to 150 °C.

Table 1
The physical properties of different samples.

Sample	S_{BET} ($m^2\ g^{-1}$)	Total pore volume ($mL\ g^{-1}$)	External surface area ($m^2\ g^{-1}$)	Mesopore volume ($mL\ g^{-1}$)	Acid density ($mmol\ g^{-1}$)[a]	Sulfur content ($mmol\ g^{-1}$)[b]
H-USY	427	0.31	77	0.12	0.26	–
H-USY-meso	429	0.34	121	0.17	0.09	–
H-USY-meso-SO_3H	330	0.29	95	0.16	0.40	0.16
H-USY-SO_3H	70	0.08	32	0.06	0.29	0.65

[a] Determined by NaOH titration.
[b] Determined by ICP-AES.

Subsequently, the TRS yield decreases with further increase of the reaction temperature because the transformation of the produced sugars to other byproducts easily occurs at high temperature.

Water at temperature above 150 °C, described as hot-compressed water, will release more H^+ and OH^- (Yang, Kobayashi, & Fukuoka, 2011). To minimize the effect of H^+ generated from water dissociation, the reaction temperature was set at 140 °C to investigate the effect of the reaction time on the yield of TRS (Fig. 2b). The yield of TRS goes up with prolonging the time, reaches a maximum of 78% at 9 h, and then decreases with further increase of time. So, the reaction time of 9 h is proper to achieve the high yield of TRS over H-USY-meso-SO_3H.

Fig. 3 shows the influence of catalyst amount on the yield of TRS. The yield of TRS increases first and then decreases with the increase of catalyst amount. With only 12.5 wt.% of catalyst, as high as 65% of TRS yield can be obtained. A maximum TRS yield (78%) is achieved at 50 wt.% of catalyst. The decrease of the TRS yield in the presence of large amount of catalyst is probably due to excess active sites inducing side reactions.

Fig. 4 exhibits the influence of hemicellulose amount on the yield of TRS. 88% yield of TRS is obtained when the weight ratio of hemicellulose/catalyst is 0.5. With the increase of the ratio to 1.0, the yield of TRS decreases to 78%. The yield of TRS does not change with further increase of the ratio to 2.0. When the ratio is increased to 4.0, 68% yield of TRS can still be obtained.

After the first reaction run using H-USY-meso-SO_3H as catalyst at 140 °C for 9 h, the catalyst was filtered, washed with deionized water to remove sugars adsorbed, dried overnight at 120 °C. The regenerated catalyst was used for the second run using 0.15 g hemicellulose as material under same reaction conditions described in Fig. 4. After the same reprocessing, the catalyst was studied in the next two runs (Fig. 5). Lost catalyst for one recycling is about 5% due to the loss during filtration. Although the yield of TRS decreases a little, the regenerated catalyst is still effective after four repeated experiments. At the fourth run, the yield of TRS is above 60%. The sulfur content of recycled catalyst was detected by ICP-AES. The content of sulfur is almost unchanged, implying that C—S bond is stable in the reaction.

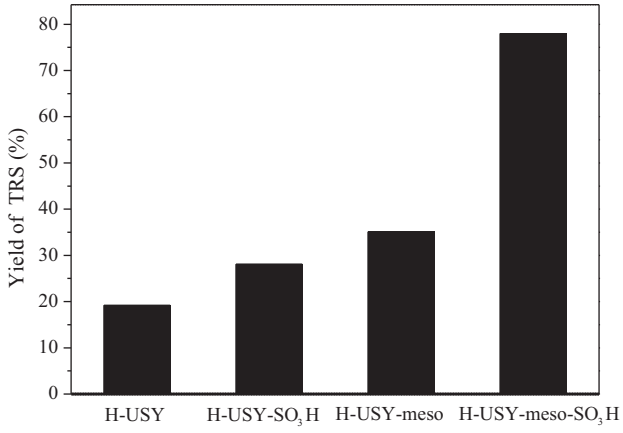

Fig. 1. The yield of TRS in the hydrolysis of hemicellulose over different catalysts. Reaction conditions: hemicellulose (0.3 g), catalyst (0.15 g), water (30 mL), 140 °C, 9 h, 1.0 MPa N_2.

3.2.2. Hydrolysis of cellulose

Cellulose, the most abundant form of biomass (40–50%), is saccharide polymers linked by β-1,4-glycosidic bonds. However, the higher degree of polymerization, crystalline structure and plenty of hydrogen bonds make cellulose difficult to hydrolysis (Mäki-Arvela, Salmi, Holmbom, Willför, & Murzin, 2011). Thus, hydrolysis of cellulose requires severe conditions, such as the use of dilute

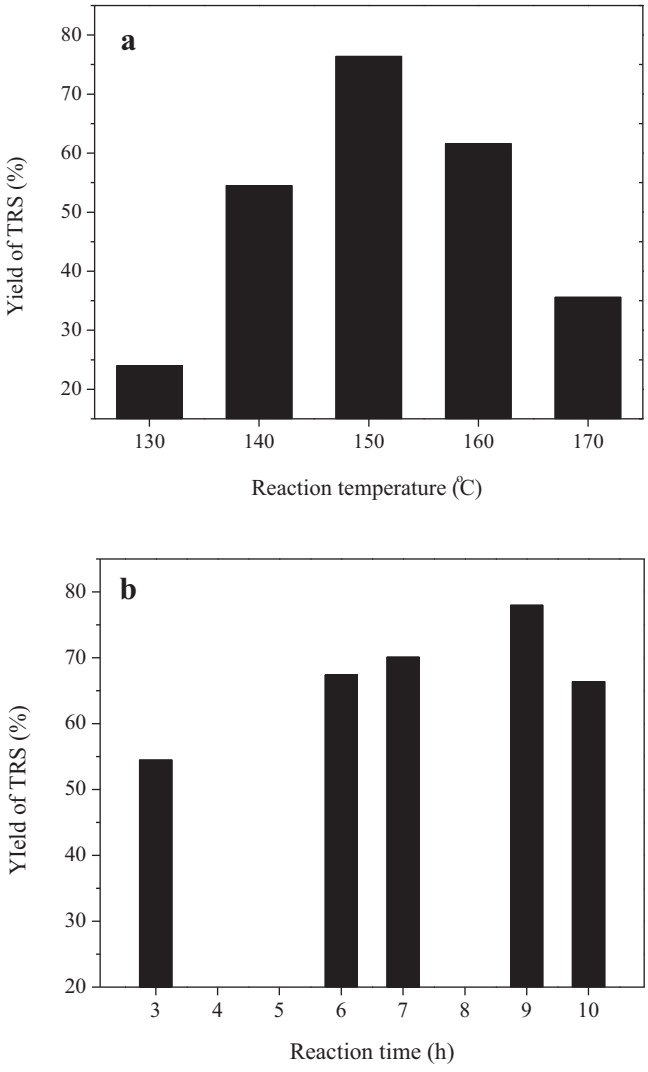

Fig. 2. Effect of the reaction temperature (a) and time (b) on the yield of TRS in the hydrolysis of hemicelluloses catalyzed by H-USY-meso-SO_3H. Reaction conditions: hemicellulose (0.3 g), catalyst (0.15 g), water (30 mL), 1.0 MPa N_2. (a) 3 h and (b) 140 °C.

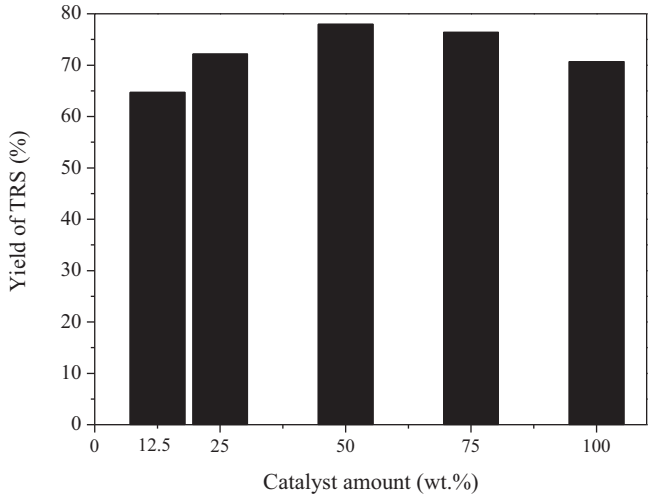

Fig. 3. Effect of the catalyst amount on the yield of TRS in the hydrolysis of hemicellulose catalyzed by H-USY-meso-SO_3H. Reaction conditions: hemicellulose (0.3 g), water (30 mL), 140 °C, 9 h, 1.0 MPa N_2. Catalyst amount is based on the weight of hemicellulose.

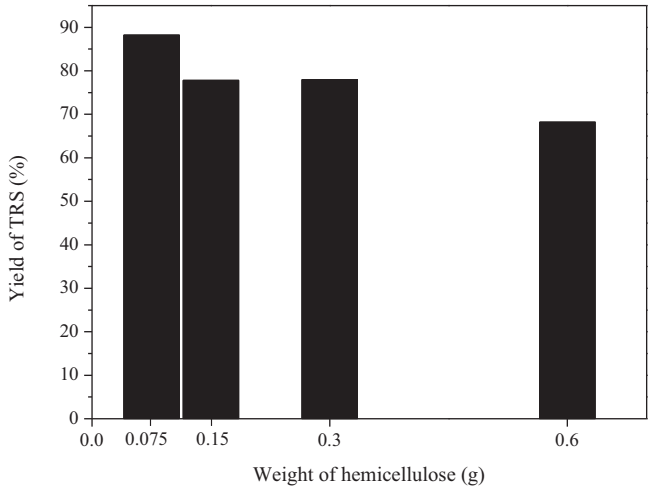

Fig. 4. Effect of hemicellulose amount on the yield of TRS in the hydrolysis of hemicellulose catalyzed by H-USY-meso-SO_3H. Reaction conditions: catalyst (0.15 g), water (30 mL), 140 °C, 9 h, 1.0 MPa N_2.

sulfuric acid at high temperatures. When using solid acid as catalyst, high acidity and large external surface area are beneficial for hydrolysis of cellulose.

Firstly, H-USY was studied for hydrolysis of α-cellulose (Table 2). Low yields of TRS and glucose are given (entry 1). Hierarchical H-USY-meso samples show higher catalytic performance than H-USY (entries 2–4). Increasing the concentration of oxalic acid for

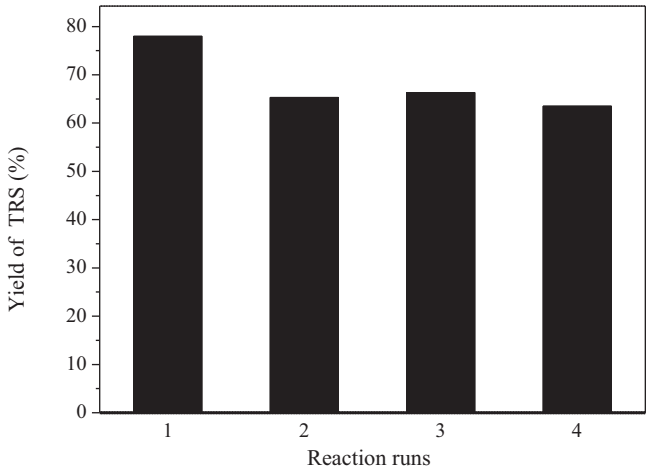

Fig. 5. Recycling study of H-USY-meso-SO_3H in the hydrolysis of hemicellulose.

treatment of H-USY, the yield of TRS first increases and reaches a maximum at 0.2 mol L^{-1}. The yield of TRS drops with further increasing the concentration to 0.3 mol L^{-1}. This change trend is similar with the hydrolysis of hemicellulose catalyzed by these catalysts in our recent report (Zhou et al., 2013). From above results, it can be seen that the catalytic activity of zeolite can be improved by introduction of meso/macropores. However, the yield of glucose is yet unsatisfactory because the introduction of large amount of meso/macropores decreased the acidity of H-USY drastically. Therefore, it is necessary to improve the acidity of the hierarchical H-USY zeolite. As expected, the conversion of α-cellulose and the yields of TRS and glucose were improved obviously using H-USY-meso-SO_3H as catalyst (entry 5). The yield of TRS and glucose is 5.1% and 2.4% over H-USY-meso-SO_3H with MCC as material, respectively (entry 6). The lower reactivity of MCC than α-cellulose is ascribed to its high crystallinity. The activity of H-USY-SO_3H is lower than H-USY-meso-SO_3H for hydrolysis of α-cellulose, which further confirms that both the acidity and the pore structure determine the activity of zeolite as catalyst in hydrolysis of biomass.

Subsequently, we optimized the reaction conditions for hydrolysis of α-cellulose catalyzed by H-USY-meso-SO_3H (Table 3). With the increase of the reaction temperature, the conversion of α-cellulose increases steadily (entries 1–3). The yield of TRS increases notably from 150 °C to 170 °C. With further increasing the temperature, the improvement of TRS is slight due to the fast decomposition of TRS at high temperature. The yield of glucose increases obviously with increasing temperature. 22.4% yield of glucose can be obtained at reaction temperature of 180 °C. Therefore, 180 °C is proper for hydrolysis of α-cellulose. With the increase of reaction time at 180 °C (entries 3–5), the conversion of α-cellulose and the yield of glucose improve obviously at initial stage. Then the activity of the catalyst reaches a platform with

Table 2
The results of different hierarchical H-USY zeolites in hydrolysis of α-cellulose.[a]

Entry	Catalyst[b]	Conversion of cellulose (%)	Yield of TRS (%)	Yield of glucose (%)
1	H-USY	12.7	3.7	0.4
2	H-USY-meso-0.1	24.4	5.4	0.8
3	H-USY-meso-0.2	24.9	11.1	1.1
4	H-USY-meso-0.3	24.6	6.5	0.4
5	H-USY-meso-SO_3H	44.6	15.7	4.2
6[c]	H-USY-meso-SO_3H	31.3	5.1	2.4
7	H-USY-SO_3H	32.0	8.6	3.7

[a] Reaction conditions: α-cellulose (0.3 g), catalyst (0.3 g), water (30 mL), 150 °C, 8 h, 1.0 MPa N_2.
[b] The number in the catalyst names denotes the concentration of oxalic acid for treatment of H-USY to obtain hierarchical H-USY. H-USY-meso-SO_3H is prepared using H-USY-meso-0.2 as precursor.
[c] MCC was used.

Table 3
Hydrolysis of α-cellulose catalyzed by H-USY-meso-SO_3H under different reaction conditions.[a]

Entry	Time (h)	Temperature (°C)	α-Cellulose (g)	Conversion of cellulose (%)	Yield of TRS (%)	Yield of glucose (%)
1	8	150	0.30	44.5	15.7	4.2
2	8	170	0.30	50.4	22.1	13.6
3	8	180	0.30	60.7	22.8	22.4
4	4	180	0.30	53.8	23.0	13.2
5	6	180	0.30	60.8	24.0	22.4
6	6	180	0.60	44.5	23.1	19.8
7	6	180	0.75	43.7	21.7	18.1
8	6	180	0.90	41.0	20.7	16.5
9	6	180	1.20	38.1	20.4	15.1
10[b]	6	180	0.30	44.7	15.8	15.1

[a] Reaction conditions: catalyst (0.3 g), water (30 mL), 1.0 MPa N_2.
[b] MCC was used.

further increase of the reaction time from 6 h to 8 h. So, the reaction time of 6 h is suitable in view of energy-consumption. The influence of the amount of α-cellulose is shown in Table 3, entries 5–9. The conversion of α-cellulose and the yields of TRS and glucose decrease slightly with increasing the amount of α-cellulose. The reaction results are still satisfying even when the weight ratio of α-cellulose/catalyst was increased to 4. Here, the conversion of α-cellulose and the yield of TRS and glucose is 38.1%, 20.4%, 15.1%, respectively. Using MCC as substrate, 44.7% conversion with glucose yield of 15.1% is obtained over H-USY-meso-SO_3H (entry 10). Similar results were reported using aryl sulfonic acid as homogenous catalyst in hydrolysis of cellulose (Amarasekara & Wiredu, 2012). It discloses that sulfonated hierarchical H-USY zeolite is an efficient catalyst for hydrolysis of biomass.

4. Conclusions

Sulfonated hierarchical H-USY zeolite was successfully synthesized by the graft method. The acidity of sulfonated hierarchical H-USY zeolite is greatly improved, which can efficiently catalyze the hydrolysis of hemicellulose and cellulose. For hydrolysis of hemicellulose, 78% yield of TRS is obtained. For hydrolysis of α-cellulose and microcrystalline cellulose, 22.4% and 15.1% yield of glucose is achieved, respectively. It implies that sulfonated hierarchical H-USY zeolite is an efficient catalyst for the hydrolysis of biomass. The hydrolysis of natural lignocelluloses catalyzed by the sulfonated hierarchical zeolites is currently under investigation.

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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.carbpol.2013.05.074.

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