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Mesoporous H-ZSM-5 as an efficient catalyst for conversions of cellulose and cellobiose into methyl glucosides in methanol

Laiqi Xue[a,b], Kang Cheng[a], Hongxi Zhang[b], Weiping Deng[a,*], Qinghong Zhang[a], Ye Wang[a,*]

[a] State Key Laboratory of Physical Chemistry of Solid Surfaces, Collaborative Innovation Center of Chemistry for Energy Materials, National Engineering Laboratory for Green Chemical Productions of Alcohols, Ethers and Esters, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, Fujian, China
[b] Department of Chemistry and Applied Chemistry, Changji University, Changji 831100, Xinjiang, China

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ABSTRACT

The alcoholysis of cellobiose, which is a dimer of glucose and a model molecule of cellulose, has been studied in methanol medium in the presence of various solid acids. Zeolite H-ZSM-5 was found to be highly efficient for the conversion of cellobiose into methyl glucosides (including methyl-α-glucoside and methyl-β-glucoside) in methanol. The Brønsted acidity plays a key role in the catalytic alcoholysis of cellobiose. H-ZSM-5 with a lower Si/Al ratio (20) possessed higher density of acidic sites afforded a higher methyl glucoside yield (53%) for the conversion of cellobiose at 423 K. The introduction of mesoporosity into the zeolite significantly enhanced its catalytic performance. Methyl glucosides with a yield of 73% were achieved from cellobiose over a mesoporous H-ZSM-5 (H-meso-ZSM-5-0.5 M) sample with an average mesopore size of 6.1 nm. The mesoporous ZSM-5 could also catalyze the direct transformation of cellulose in methanol, providing methyl glucosides with yields of 51% at 463 K. Our comparative studies revealed that the alcoholysis of cellulose in methanol proceeded more efficiently than the hydrolysis of cellulose in water under similar reaction conditions.

1. Introduction

Catalytic transformation of renewable and inedible lignocellulosic biomass into chemicals and fuels represents a promising route for establishing the sustainable chemistry society [1–8]. Cellulose is the most abundant component in the lignocellulosic biomass. The efficient conversion of cellulose into chemicals is of essential importance for the utilization of lignocellulosic biomass and has attracted much attention in recent years [3,5,6,8–12]. Cellulose is a crystalline polymer of D-glucose linked by β-1,4-glycosidic bonds. Because of such linkage and the presence of numerous hydroxyl groups, there exist extensive hydrogen-bonding networks in cellulose, making the crystalline structure of cellulose robust [8]. Therefore, the selective transformation of cellulose into target products under mild conditions is highly challenging.

Cellulase enzymes are known to catalyze the hydrolysis of cellulose with high efficiency under mild conditions [13]. However, this enzymatic process is limited by the high cost of enzyme, low productivity, and complex handling procedure. Thus, many studies have been devoted to the development of chemocatalytic processes for the hydrolysis of cellulose. Although mineral acids (e.g., H_2SO_4 and HCl) showed high performances for the hydrolysis of cellulose, these homogeneous systems still suffer from problems of the product/catalyst separation, reactor corrosion, catalyst recycling, and treatment of waste effluents. Solid acid catalysts such as carbon materials bearing SO_3H groups [14–17], sulfonated resins or metal oxides [18–20], layered metal oxides [21], phosphates [22], and modified graphene oxides [23] have been reported for the hydrolysis of cellulose. High yields of glucose could be attained by using solid materials bearing SO_3H groups with strong acidity. However, severe leaching of the SO_3H groups occurred in most cases under hydrothermal conditions. Moreover, because of the presence of highly reactive groups (i.e., aldehyde and hydroxyls), glucose is unstable in hot water. Many side reactions, including isomerization, dehydration, rehydration, retro-aldol, and polymerization, may take place, thereby significantly decreasing the selectivity

* Corresponding authors. Fax: +86 592 2183047.
E-mail addresses: dengwp@xmu.edu.cn (W. Deng), wangye@xmu.edu.cn (Y. Wang).

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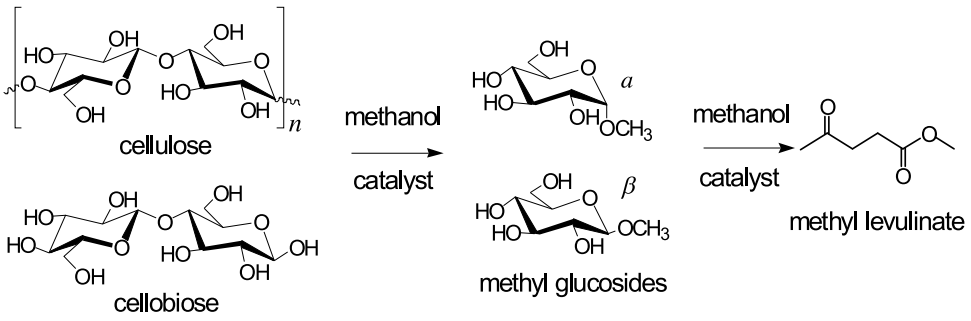

Scheme 1. Conversions of cellulose and cellobiose into methyl glucosides in methanol.

of glucose. In this context, one promising strategy is to develop bi- or multifunctional catalysts for the transformation of cellulose into more stable and valuable chemicals such as polyols [24–30], gluconic acid [31,32], and hydroxymethylfurfural (HMF) [33,34] through glucose intermediate. For instance, noble metals (e.g., Pt and Ru) in combination with solid materials containing acidic sites (e.g., γ-Al_2O_3, carbon nanotubes, and polyoxometalates) were used as bifunctional catalysts to catalyze the hydrolysis-hydrogenation of cellulose to sorbitol and mannitol [24–26]. The reversibly generated H_3O^+ in hot water combined with Ru/AC (AC: activated carbon) could also convert cellulose into sorbitol [27]. The tungsten-based catalysts with C—C bond cleavage function were used to catalyze the conversion of cellulose into ethylene or propylene glycols [28–30].

In our previous work, we proposed a strategy to increase the selectivity of monosaccharides by using alcohol medium instead of water medium. We demonstrated that cellulose could be converted efficiently to methyl or ethyl glucosides (including α- and β- isomers) in methanol or ethanol in the presence of Keggin-type heteropolyacids (i.e., $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$) [35,36]. Besides methanol and ethanol, long chain alcohols were also employed for the alcoholysis of cellulose. For example, by using ionic liquids (ILs) as solvents, Corma and co-workers succeeded in the transformation of cellulose into butyl-, hexyl-, octyl-, decyl-, and dodecyl-glycosides in the presence of an acidic resin catalyst (i.e., Amberlyst-15) [37,38]. The highest octyl-glycoside yield could reach 82% after a reaction at 363 K for 1.5 h [37]. A catalyst combining an IL with polyoxometalates, i.e., polyvinylpyrrolidone-stabilized heteropolyacid (PVP–HPA), was demonstrated to be efficient for the alcoholysis of cellulose in butanol [39]. This combined catalytic system provided >87% conversion of cellulose and ~90% selectivity of butyl glucosides at 428 K. However, the gradual leaching of acid sites occurred during the reaction. ILs are effective to dissolve cellulose and can enhance the alcoholysis, but they are still expensive, making their practical application less attractive. The use of a cheaper alcohol as the reaction medium for the production of alkyl glucosides is a promising route for the practical transformation of cellulose. The development of stable and efficient heterogeneous catalysts for the alcoholysis of cellulose under mild conditions remains a challenging goal.

The present work contributes to the development of heterogeneous catalysts for the efficient alcoholysis of cellulose and cellobiose to methyl glucosides (including methyl-α-glucoside and methyl-β-glucoside) in methanol under mild conditions (Scheme 1). We will show that zeolite H-ZSM-5 is an excellent solid acid catalyst for the catalytic conversion of cellobiose. The effect of acidity on catalytic performances will be investigated by changing the Si/Al ratio in H-ZSM-5. Moreover, hierarchical zeolites containing both micropores and mesopores, which combine the advantages of zeolites (with strong acidity and high stability) and mesoporous materials (with efficient mass transportation), have attracted much attention for the conversion of larger molecules in recent years [40,41]. We synthesized mesoporous ZSM-5 and mesoporous Y zeolites, and demonstrated that these mesoporous zeolites were promising for Fischer–Tropsch synthesis [42–44]. Since cellobiose and cellulose are relatively large molecules, we expect that the hierarchical zeolites would be suitable for the conversions of these molecules. In the present work, we will investigate the effect of mesoporosity as well as acidity of ZSM-5-based catalysts on their catalytic behaviors for the conversions of cellobiose and cellulose.

2. Experimental

2.1. Catalyst preparation

Cellobiose and cellulose were obtained from J&K Chemicals. SiO_2, Al_2O_3, and $H_3PW_{12}O_{40}$ were purchased from Alfa Aesar. Zeolites including H-ZSM-5, H-MOR, H-MCM-22, and H-Y were purchased from Nankai University Catalyst Co. Mesoporous ZSM-5 samples were prepared by treating the parent Na-ZSM-5 with aqueous solutions of NaOH with different concentrations [43]. The desilication occurred and the samples with different mean sizes of mesopores could be obtained [43]. The Na-form mesoporous zeolites were then exchanged to their H-forms by a typical ion-exchange method with an aqueous solution of NH_4NO_3 (concentration, 1.0 M), followed by drying and calcination in air at 823 K. The obtained samples were subsequently subjected to acid treatment in an aqueous solution of HNO_3 (concentration, 0.1 M) at 338 K for 6 h to remove the non-framework aluminium species possibly formed during the desilication process. The finally obtained samples were denoted as H-meso-ZSM-5-*x*M, where *x* was the concentration of NaOH aqueous solution.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were recorded on a Panalytical X'pert Pro Super X-ray diffractometer with Cu Kα radiation (40 kV and 30 mA). Transmission electronic microscopy (TEM) measurements were carried out on a JEM-2100 electron microscope operated at an acceleration voltage of 200 kV. Nitrogen physisorption at 77 K was performed with a Micromeritics ASAP 2010 M instrument. The sample was pretreated at 573 K in vacuum for 3 h prior to N_2 adsorption. The surface area was calculated using the Brunauer–Emmett–Teller (BET) method in a pressure range of P/P_0 = 0.05–0.3. The pore size distribution in the mesoporous region was determined by the Barrett–Joyner–Halenda (BJH) method [45] and that in the microporous region was evaluated by the Horváth–Kawazoe (HK) method [46]. The microporous volume was estimated by the *t*-plot method [47].

The ammonia temperature-programmed desorption (NH_3-TPD) was performed on a Micromeritics AutoChem 2920 II instrument.

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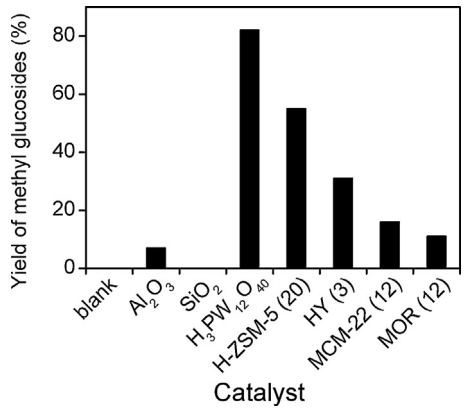

Fig. 1. Yields of methyl glucosides in the conversion of cellobiose with different catalysts. Reaction conditions: W(cellobiose) = 0.20 g, W(catalyst) = 0.050 g, $V(CH_3OH)$ = 20 mL, $P(N_2)$ = 3 MPa, T = 423 K, t = 4 h. The number in the parenthesis denotes the Si/Al ratio.

Typically, the sample loaded in a quartz reactor was first pretreated with He at 623 K for 1 h. After the sample was cooled to 373 K in He gas flow, NH_3 adsorption was performed by switching the He flow to a NH_3–He (10 vol% NH_3) gas mixture and then keeping at 373 K for 1 h. The gas phase or the weakly adsorbed NH_3 was purged by high-purity He at the same temperature. NH_3-TPD was performed in the He flow by raising the temperature to 973 K at a rate of 10 K min^{-1}, and the desorbed NH_3 molecules were detected by ThermoStar GSD 301 T2 mass spectrometer with the signal of m/e = 16.

2.3. Catalytic reaction

The conversions of cellulose and cellobiose were performed in a Teflon-lined stainless-steel autoclave with a volume of 75 cm^3. After the catalyst (typically 0.050 g) and cellobiose (typically 0.20 g, equivalent to 1.2 mmol $C_6H_{10}O_5$ unit) were added into the autoclave pre-charged with methanol (typically 20 cm^3), N_2 with a pressure of 3.0 MPa was introduced. The reaction was started by heating the mixture to a reaction temperature. After a certain time (4 h), the reaction was stopped by cooled water, and the products were analyzed by HPLC (Shimazu LC-20A) equipped with a RI detector and a Shodex™ SH1011 column (10 μm, 6.5 × 300 mm). The conversion of cellulose was calculated by the change of the weight of cellulose after the reaction. The yield of a product was defined as the percentage of the molar amount of the target product in the total molar amount of $C_6H_{10}O_5$ unit in cellulose or cellobiose.

3. Results and discussion

3.1. Catalytic behaviors of H-ZSM-5 for the conversion of cellobiose in methanol

We investigated the catalytic performances of metal oxides (i.e., SiO_2, Al_2O_3), zeolites (H-ZSM-5, H-MOR, MCM-22, H-Y), and a heteropolyacid ($H_3PW_{12}O_{40}$) for the conversion of cellobiose in methanol at 423 K. No products were observed in absence of a catalyst. Among the catalysts investigated, the Keggin-type $H_3PW_{12}O_{40}$, a strong Brønsted acid, showed the highest yield of methyl glucosides (82%, including α and β isomers) from cellobiose (Fig. 1). High activities of heteropolyacid in the conversions of cellobiose and cellulose were already reported in our previous papers [35,36]. Although promising, $H_3PW_{12}O_{40}$ is highly soluble in methanol, and this makes its recovery and isolation from the reaction solution not easy. It is of interest that the solid catalysts displayed in Fig. 1 except for SiO_2, which does not possess acidity, can also catalyze the conversion of cellobiose into methyl glucosides. H-form zeolites including H-ZSM-5, H-Y, H-MCM-22, and H-MOR with Brønsted acidity were more efficient for the formation of methyl glucosides from cellobiose than Al_2O_3, which possessed mainly Lewis acidity. Among all the solid acid catalysts investigated, H-ZSM-5 afforded the highest yield to methyl glucosides (53%). H-Y, H-MCM-22, and H-MOR produced methyl glucosides with yields of 10–30% under the same reaction conditions.

Table 1
Conversion of cellobiose catalyzed by H-ZSM-5 with different Si/Al ratios.

Catalysts[a]	Density of acid sites[b] (mmol g^{-1})	Conv. (%)	Yield[c] (%)		TON[d]
			M-β-G	M-α-G-GML	
Blank	–	<5	0	0	0 –
H-ZSM-5 (20)	0.46	61	18	35	3.16.7
H-ZSM-5 (50)	0.25	50	13	24	2.68.6
H-ZSM-5 (80)	0.24	43	10	22	2.27.8
H-ZSM-5 (120)	0.14	30	4.2	11	0 6.3
H-ZSM-5 (260)	0.07	11	1.6	3.6	0 4.3

Reaction conditions: W(cellobiose) = 0.20 g, W(catalyst) = 0.10 g, $V(CH_3OH)$ = 20 mL, $P(N_2)$ = 3 MPa, T = 423 K, t = 4 h.
[a] The number in the parenthesis after H-ZSM-5 denotes the Si/Al ratio.
[b] Evaluated from NH_3-TPD results in Fig. 2.
[c] M-α-G, M-β-G, and ML denote methyl-α-glucoside, methyl-β-glucoside, and methyl levulinate, respectively.
[d] TON was calculated by the mole of methyl glucosides formed per mole of acid sites.

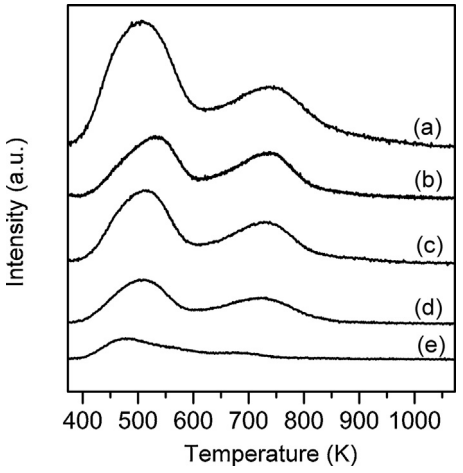

Fig. 2. NH_3-TPD profiles of H-ZSM-5 samples with different Si/Al ratios. (a) H-ZSM-5 (20), (b) H-ZSM-5 (50), (c) H-ZSM-5 (80), (d) H-ZSM-5 (200), (e) H-ZSM-5 (260). The number in the parenthesis denotes the Si/Al ratio.

To gain insights into the role of acidity, we investigated the catalytic performances of H-ZSM-5 samples with different Si/Al ratios for the transformation of cellobiose in methanol. As shown in Table 1, the decrease in Si/Al ratio increased the conversion of cellobiose and the yields of both methyl α- and β-glucosides. A higher yield of methyl glucosides was attained over H-ZSM-5 with a lower Si/Al ratio. Over the H-ZSM-5 with a lower Si/Al ratio (20–80), methyl levulinate was also formed as a by-product. This suggests the occurrence of the consecutive degradation of methyl glucosides (Scheme 1).

We characterized the acidity of H-ZSM-5 samples with different Si/Al ratios by NH_3-TPD. Fig. 2 displays that all the H-ZSM-5 samples exhibit two NH_3 desorption peaks at around 500 K and 750 K. The lower and higher temperature desorption peaks could be assigned to hydrogen-bonded NH_3 molecules and the NH_3 molecules chemisorbed on Brønsted acid sites, respectively [48]. The intensities of both peaks decreased markedly with increasing

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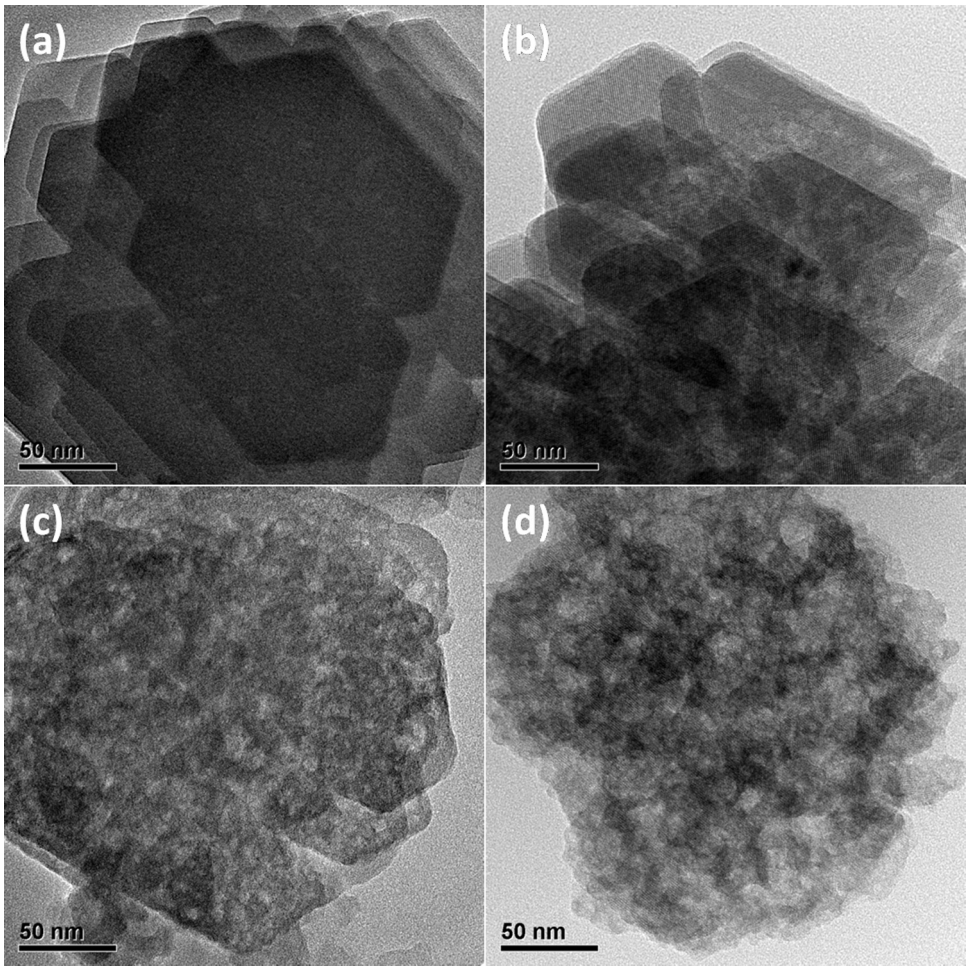

Fig. 3. TEM images. (a) H-ZSM-5, (b) H-meso-ZSM-5-0.3 M, (c) H-meso-ZSM-5-0.5 M, (d) H-meso-ZSM-5-1.0 M.

the Si/Al ratio, indicating a decrease in the density of acid sites. Since the Brønsted acid sites would play key roles in the conversion of cellobiose or cellulose, we have estimated the density of Brønsted acid sites on the H-ZSM-5 sample from the high temperature peak in NH_3-TPD profiles. As displayed in Table 1, the density of Brønsted acid sites decreased gradually from 0.46 to 0.07 mmol g^{-1} with an increase in the Si/Al ratio from 20 to 260. The correlation of this trend with that for the catalytic performance (Table 1) suggests that the Brønsted acid site is responsible for the conversion of cellobiose. Based on the density of the Brønsted acid site, we have further calculated the turnover number (TON) for the formation of methyl glucosides, i.e., the moles of methyl glucosides formed per mole of acidic sites, for each H-ZSM-5 catalyst. The result listed in Table 1 shows that the TON was in a range of 6.3–8.6 except for the sample with a Si/Al ratio of 260.

3.2. Synthesis and characterizations of mesoporous H-ZSM-5

It is known that the Brønsted acid sites are predominantly located inside the micropores of zeolites. The micropore size of H-ZSM-5 (~0.55 nm) is close to the diameter of a glucose unit (~0.58 nm). The diffusion of cellobiose, which is a dimer of glucose, into the micropores of H-ZSM-5 may be limited. This may limit the increase in the yield of methyl glucosides over the H-ZSM-5 with a higher density of Brønsted acid sites. Actually, the TON for the H-ZSM-5 with a Si/Al ratio of 20 became lower than that for the

Table 2
Textural properties of mesoporous H-ZSM-5.

Sample	S_{BET}[a] (m^2g^{-1})	S_{micro}[b] (m^2g^{-1})	S_{exter}[c] (m^2g^{-1})	S_{meso}[d] (m^2g^{-1})	V_{total}[e] (cm^3g^{-1})	V_{micro}[f] (cm^3g^{-1})	V_{meso}[g] (cm^3g^{-1})	D_{meso}[h] (nm)
H-ZSM-5	354	304	50	29	0.18	0.13	0.04	–
H-meso-ZSM-5-0.3M	373	241	132	116	0.23	0.11	0.13	4.2
H-meso-ZSM-5-0.5M	416	241	175	164	0.33	0.11	0.25	6.1
H-meso-ZSM-5-1.0M	395	210	186	196	0.49	0.10	0.46	13

[a] BET surface area.
[b] Microporous surface area evaluated by the *t*-plot method.
[c] External surface area evaluated by the *t*-plot method.
[d] Mesoporous surface area valuated by the BJH method.
[e] Total pore volume evaluated by the single-point desorption at $P/P_0 = 0.975$.
[f] Microporous volume evaluated by the *t*-plot method.
[g] Mesoporous volume evaluated by the BJH method.
[h] Mean pore diameter for mesopores evaluated by the BJH method.

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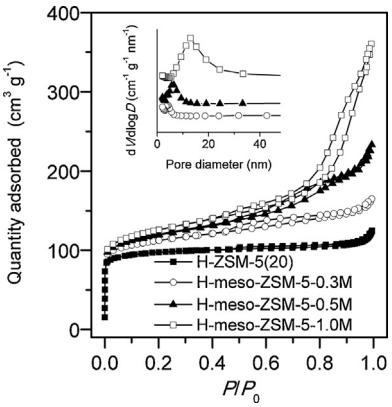

Fig. 4. N_2 adsorption-desorption isotherms and pore size distributions (inset) for the H-ZSM-5 and mesoporous H-meso-ZSM-5 (20)-*x*M samples.

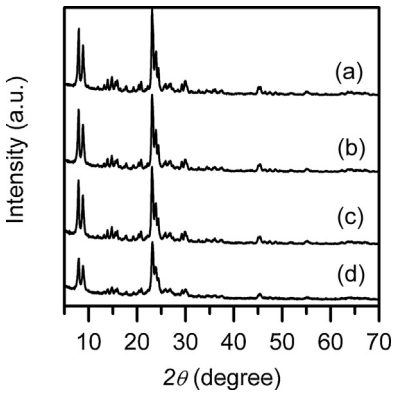

Fig. 5. XRD patterns. (a) H-ZSM-5, (b) H-meso-ZSM-5-0.3 M, (c) H-meso-ZSM-5-0.5 M, (d) H-meso-ZSM-5-1.0 M.

sample with a Si/Al ratio of 50. Thus, the introduction of mesoporosity would be helpful in enhancing the catalytic performance by accelerating the diffusions of reactants and products.

We synthesized mesoporous ZSM-5 samples with different mesopore sizes by post-treating crystalline Na-ZSM-5 with a Si/Al ratio of 20 in NaOH aqueous solutions with different concentrations at 343 K, followed by ion exchange to transform the Na-form samples into H-form samples. The H-form mesoporous samples were denoted as H-meso-ZSM-5-*x*M, where *x* was the concentration of aqueous NaOH solution used for post-treatment. Fig. 3 shows typical TEM micrographs for H-ZSM-5 and H-meso-ZSM-5 samples. H-ZSM-5 crystals possess plate-like morphology. The post-treatment with aqueous NaOH solutions resulted in the generation of mesopores in ZSM-5 crystals. The sizes of mesopores increased with an increase in the NaOH concentration.

To gain more information about the porous property of the mesoporous ZSM-5, we performed N_2 physisorption measurements. Fig. 4 displays the N_2 adsorption/desorption isotherms of mesoporous H-ZSM-5 samples together with H-ZSM-5. H-ZSM-5 exhibits the type I isotherm, which is typical of a microporous zeolite. After treating ZSM-5 with aqueous NaOH solutions, the isotherms of samples gradually changed from the type I to the type IV, and hysteresis loops were observed. This clearly suggests the generation of mesopores. By using the BJH method, we evaluated the pore-diameter distribution in mesoporous region for the H-meso-ZSM-5-*x*M samples. Relatively narrow pore-diameter distributions were observed for the samples with $x = 0.3$ and 0.5 (inset figure in Fig. 4). The average size of mesopores depended on the concentration of NaOH used for post-treatment. A higher concentration of NaOH resulted in a larger average size of mesopores. With an increase in *x* value from 0.3 to 1.0, the average size of mesopores increased from 4.2 to 13 nm (Table 2). The pore volumes and surface areas of the H-meso-ZSM-5-*x*M samples were also evaluated from N_2 physisorption measurements. The increase in the concentration of NaOH aqueous solution led to a decrease in the microporous volume and microporous surface area, which were estimated by the *t*-plot method [47]. Meanwhile, the mesoporous surface area and mesoporous volume, calculated by the BJH method, increased significantly (Table 2). These results further confirmed the generation of mesopores during the desilication by NaOH aqueous solutions. It should be mentioned that the mesoporous surface area was very similar to the external surface area evaluated by the *t*-plot method (Table 2), suggesting that the generation of mesopores mainly contributed to the increase in the external surface area.

We also investigated the change of crystalline structure of ZSM-5 after post-treatment by XRD (Fig. 5). All the diffraction peaks belonging to crystalline ZSM-5 could be observed for H-meso-ZSM-5-*x*M samples, but the intensities of the diffraction peaks decreased to some extent when the NaOH aqueous solution with a concentration of 1.0 M was used for the post-treatment (Fig. 5d). Therefore, the crystalline structure of ZSM-5 was maintained for the H-meso-ZSM-5-*x*M samples, although the regularity of the long-range order decreased for the sample treated by 1.0 M NaOH.

Our NH_3-TPD measurements for the H-meso-ZSM-5-*x*M samples revealed that, similar to H-ZSM-5, these samples also exhibited two NH_3 desorption peaks at around 500 K and 750 K (Fig. 6). The increase in the concentration of NaOH used for post-treatment slightly decreased the intensity of the peak at 750 K, which could be ascribed to the desorption of NH_3 chemisorbed on the Brønsted acid sites. Using NH_3-TPD results, we estimated the density of Brønsted acid sites. The result showed that the density of Brønsted acid sites was in a range of 0.41–0.49 mmol g^{-1} for the H-meso-ZSM-5-*x*M samples (Table 3), which was comparable to that for H-ZSM-5. Thus, the Brønsted acidity of the H-meso-ZSM-5-*x*M samples was almost sustained after the introduction of mesopores though the post-treatment with NaOH aqueous solutions.

Table 3
Catalytic performances of mesoporous H-ZSM-5 with different mesopore sizes for the conversion of cellobiose.

Catalysts	Mesopore (nm)	Density of acid sites[a] (mmol g^{-1})	Conv. (%)	Yield[b] (%)			TON[c]
				M-β-G	M-α-G	ML	
H-ZSM-5	–	0.46	61	18	35	3.1	6.7
H-meso-ZSM-5-0.3M	4.2	0.49	70	20	38	2.4	6.9
H-meso-ZSM-5-0.5M	6.1	0.44	83	27	46	3.2	9.7
H-meso-ZSM-5-1.0M	13	0.41	90	25	49	2.2	10

Reaction conditions: *W*(cellobiose) = 0.20 g, *W*(catalyst) = 0.10 g, *V*(CH_3OH) = 20 mL, *P*(N_2) = 3 MPa, *T* = 423 K, *t* = 4 h.
[a] Estimated from NH_3-TPD results in Fig. 6.
[b] M-α-G, M-β-G, and ML denote methyl-α-glucoside, methyl-β-glucoside, and methyl levulinate, respectively.
[c] TON was calculated by the mole of methyl glucosides formed per mole of acid sites.

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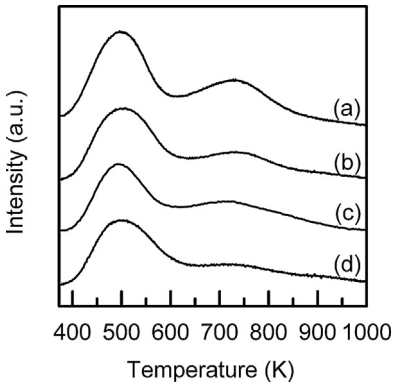

Fig. 6. NH_3-TPD profiles. (a) H-ZSM-5, (b) H-meso-ZSM-5-0.3 M, (c) H-meso-ZSM-5-0.5 M, (d) H-meso-ZSM-5-1.0 M.

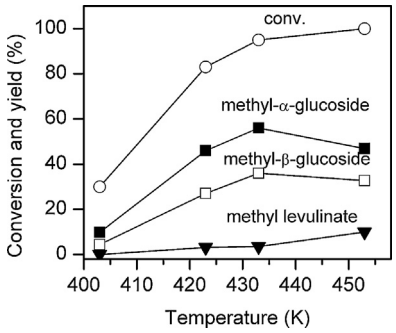

Fig. 7. Catalytic performances of H-meso-ZSM-5-0.5 M for the conversion of cellobiose at different temperatures. Reaction conditions: W(cellobiose) = 0.20 g, W(catalyst) = 0.050 g, $V(CH_3OH)$ = 20 mL, $P(N_2)$ = 3 MPa, t = 4 h.

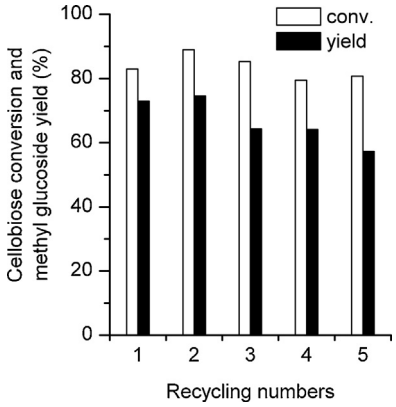

Fig. 8. Recycling uses of the H-meso-ZSM-5-0.5 M catalyst for the conversion of cellobiose. Reaction conditions: W(cellobiose) = 0.20 g, W(catalyst) = 0.10 g, $V(CH_3OH)$ = 20 mL, $P(N_2)$ = 3 MPa, T = 423 K, t = 4 h.

3.3. Catalytic behaviors of mesoporous H-ZSM-5 for the conversion of cellobiose in methanol

Table 3 displays the catalytic performances of the H-meso-ZSM-5-*x*M series of samples as well as H-ZSM-5 (Si/Al = 20) for the conversion of cellobiose in methanol at 423 K. As compared to the parent H-ZSM-5, the H-meso-ZSM-5-*x*M catalysts exhibited better activities and higher yields of methyl glucosides. With increasing the concentration of NaOH used for post-treatment, the yield of methyl glucosides increased significantly. Over the H-meso-ZSM-5-0.5 M and H-meso-ZSM-5-1.0 M catalysts, the yields of methyl glucosides reached 73% and 74%, respectively. We also calculated the TON for the formation of methyl glucosides based on the density of Brønsted acid sites obtained from NH_3-TPD measurements. As listed in Table 3, the catalyst treated with a higher concentration of aqueous NaOH solution afforded a higher TON. This suggests that the acid sites in mesoporous H-ZSM-5 work more efficiently for the transformation of cellobiose to methyl glucosides. The combination of the catalytic performances of these catalysts with their textural properties in Table 2 allows us to conclude that the catalyst with larger mesopores is beneficial to the transformation of cellobiose. The generation of mesopores, in particular the mesopores with larger average sizes (6.1 and 13 nm), may create larger amounts of acid sites located inside the mesopores but outside the micropores. These acid sites can be accessed by cellobiose molecules more facilely. The diffusion limitation can also be improved in the presence of larger mesopores. Thus, the formation of methyl glucosides can be enhanced owing to the generation of mesopores.

To gain further insights into the transformation of cellobiose in methanol over the H-meso-ZSM-5-0.5 M, we have investigated the effect of reaction temperature on catalytic performances. Fig. 7 shows that the conversion of cellobiose is only ~30% at a relatively low temperature (403 K) in methanol. The conversion increased significantly with temperature. The yield of methyl glucosides also increased with temperature and reached up to 94% at 433 K. A further increase in temperature to 453 K rather decreased the yield of methyl glucosides but increased that of methyl levulinate, indicating the transformation of methyl glucosides to methyl levulinate at higher temperatures. The yield of methyl levulinate reached 10% in the conversion of cellobiose in methanol at 453 K.

The catalyst stability is another crucial factor for solid acid catalysts. We have examined the recycling uses of the H-meso-ZSM-5-0.5 M catalyst for the conversion of cellobiose in methanol. After each run, the catalyst was recovered by filtration, washing and drying, and then was re-used in the next run. Fig. 8 shows that the conversion of cellobiose and the yield of methyl glucosides decrease slightly after repeated uses for five runs. The yield of methyl glucosides could be maintained at ~60%.

Table 4
Catalytic performances of H-ZSM-5 and H-meso-ZSM-5-0.5 M for the conversion of cellulose.

Catalyst	Time (h)	Conv. (%)	Yield[a] (%)			TON[b]
			M-β-G	M-α-G	ML	
H-ZSM-5	4	<5	0.3	0.9	0	0.15
H-ZSM-5	12	21	5.0	8.3	0.2	1.7
H-meso-ZSM-5-0.5M	6	40	10	16	1	3.6
H-meso-ZSM-5-0.5M	12	64	21	30	3.3	7.2
H-meso-ZSM-5-0.5M	18	73	11	21	8.3	4.5

Reaction conditions: W(ball-milled cellulose) = 0.10 g, W(catalyst) = 0.10 g, $V(CH_3OH)$ = 20 mL, $P(N_2)$ = 3 MPa, T = 463 K.

[a] M-α-G, M-β-G, and ML denote methyl-α-glucoside, methyl-β-glucoside, and methyl levulinate, respectively.

[b] TON was calculated by the mole of methyl glucosides formed per mole of acid sites.

3.4. Mesoporous H-ZSM-5 for the conversion of cellulose in methanol

We have further investigated the catalytic performance of the H-meso-ZSM-5-0.5 M as well as H-ZSM-5 for the conversion of ball-milled cellulose in methanol at 467 K. H-ZSM-5 exhibited a low activity at a short reaction time (4 h) (Table 4). With prolonging reaction time to 12 h, 21% of cellulose was converted, yielding ~13%

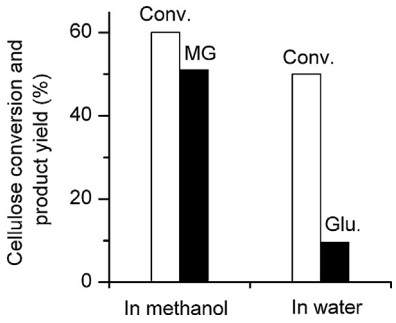

Fig. 9. Comparison of the conversion of cellulose in methanol with that in water over the H-meso-ZSM-5-0.5 M catalyst. Reaction conditions: *W*(ball-milled cellulose) = 0.10 g, *W*(catalyst) = 0.10 g, *V*(CH_3OH or water) = 20 mL, *P*(N_2) = 3 MPa, *T* = 463 K, *t* = 12 h. MG denotes the sum of methyl-α-glucoside and methyl-β-glucoside. Glu. denotes glucose.

of methyl glucosides. The H-meso-ZSM-5-0.5 M catalyst provided significantly higher cellulose conversion and methyl glucoside yield than H-ZSM-5. The yield of methyl glucosides reached 51% for the conversion of cellulose over the H-meso-ZSM-5-0.5 M catalyst at 463 K for 12 h. The TON for the mesoporous zeolite was ~4 times higher than that for the microporous zeolite in 12 h. This clearly confirms that the presence of mesopores is beneficial to the activation of glycosidic bonds in cellulose and the formation of methyl glycosides. A further increase in the reaction time raised the conversion of cellulose but decreased the yield of methyl glucosides because of the formation of methyl levulinate.

We compared the conversion of ball-milled cellulose in methanol with that in water under similar reaction conditions using the H-meso-ZSM-5-0.5 M catalyst. In water medium, glucose was formed as the major product, and a glucose yield of 10% was attained after a 12 h reaction at 463 K (Fig. 9). Fructose, 5-hydroxymethyl furfural (HMF) and humins were formed as the major by-products. The yield of methyl glucosides obtained for the conversion of cellulose in methanol (~50%) was significantly higher. This demonstrates that the employment of methanol as a reaction medium is beneficial to the selective conversion of cellulose to monosaccharides. This phenomenon can be interpreted by the fact that methyl glucosides in methanol medium are more stable against further degradations than glucose in water [35,36].

4. Conclusions

Mesoporous H-ZSM-5 is an efficient heterogeneous catalyst for the transformation of cellobiose into methyl glucosides in methanol medium. The acidity and mesoporosity are two crucial factors that influence the catalytic performance. The microporous H-ZSM-5 with a low Si/Al ratio and higher density of Brønsted acid sites exhibits a higher yield of methyl glucosides. A maximum yield of 53% has been obtained from the conversion of cellobiose with H-ZSM-5 with a Si/Al ratio of 20. The introduction of mesoporosity significantly increases the yield of methyl glucosides. The catalyst with a larger average size of mesopores shows a higher yield of methyl glucosides. The H-meso-ZSM-5-0.5 M catalyst bearing an average mesopore size of 6.1 nm affords a methyl glucoside yield of 73% for the conversion of cellobiose at 423 K for 4 h. The catalyst is also stable and can be recycled for several times. The H-meso-ZSM-5-0.5 M catalyst is also efficient for the direct conversion of cellulose, providing a methyl glucoside yield of 51% after a reaction at 463 K for 12 h. Our studies reveal that the transformation of cellulose in methanol is more efficient than that in water under similar reaction conditions. We believe that the mesoporous zeolite in combination with a cheaper alcohol medium represents a promising catalytic system for the direct transformation of cellulose under mild conditions.

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