



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



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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.

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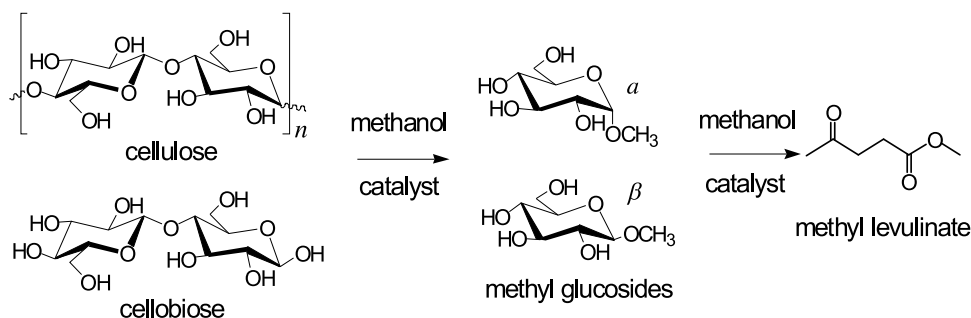
1. Introduction

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., H₂SO₄ 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 SO₃H 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 SO₃H groups with strong acidity. However, severe leaching of the SO₃H 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

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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., $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$) [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 $\text{H}_3\text{PW}_{12}\text{O}_{40}$ 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 $\text{Cu K}\alpha$ 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 2010M 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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