

## Research article

# One-pot production of 5-hydroxymethylfurfural from cellulose using solid acid catalysts



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## ABSTRACT

5-Hydroxymethylfurfural (HMF) is one of the most important intermediate platforms for production of both chemicals and liquid fuel derived from biomass. The one-pot production of HMF from cellulose was conducted in a batch reactor in the presence of various solid acid catalysts. The prepared catalysts were characterized by means of Brunauer–Emmett–Teller measurement and pyridine adsorption FT-IR to investigate their pore structure and acidic properties. The presence of gaseous hydrogen enhanced the formation of HMF by suppressing the formation of byproducts. Increasing the acid amount of the catalyst caused an increase in the conversion and selectivity for organic acid and a decrease in the HMF selectivity. A Brønsted-type catalyst (Al-SBA-15) favored the formation of HMF. The reaction conditions of 220 °C, 5 min, and a hydrogen pressure of 1 MPa resulted in the highest yield of HMF, and selectivity of 26.9% was achieved when the Al-SBA-15 catalyst was used. Moreover, under the same conditions, cellulose extracted from eucalyptus, a practical biomass, was converted to HMF in a one-pot synthesis with a yield of 13.0 C-mol.%.

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## 1. Introduction

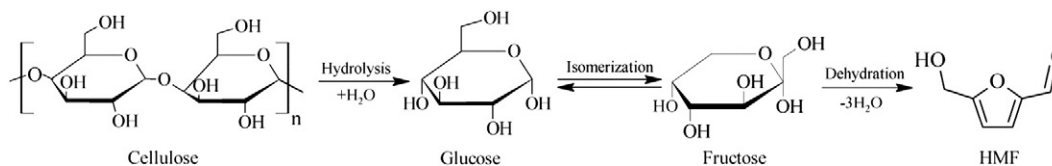
Fossil resources play an important role in product manufacturing, but they are a limited resource and will eventually be exhausted. Manufacturing chemical raw materials from biomass, a renewable resource, rather than petroleum, is an important solution. In 2004, the US Department of Energy (DOE) specified platform chemicals obtained from lignocellulosic biomass [1], which was subsequently revisited by Bozell and Petersen in 2010 [2]. 5-Hydroxymethylfurfural (HMF) was specified as one of the most important intermediate biomass-derived synthesis products and is promising for the production of biofuel such as high quality liquid fuel such as 2,5-dimethylfuran via the hydrogenation and/or hydrodeoxygenation of HMF [3]. Further, the bio-derived fuel or bio-jet oil could be directly produced via aldol condensation of furfural and HMF with cyclic ketones [4,5]. In general, HMF is formed from glucose and fructose [6], as shown in Scheme 1. First, cellulose is hydrolyzed and converted into glucose. Second, the glucose is converted into fructose through isomerization. Finally, fructose is converted into HMF through dehydration. In recent years, the direct conversion of glucose and cellulose into HMF has attracted great interest. Dumesic et al. reported a two-stage method using an aqueous solution of hydrochloric acid and an organic solvent for synthesizing HMF from glucose [7]. Zhao et al. reported nearly 70% yield of HMF from glucose in the ionic liquid 1-ethyl-3-methyl-imidazolium chloride using  $\text{CrCl}_2$  [8]. Huang et al.

achieved a 63% HMF yield by combining enzymatic and acid catalysis to synthesize HMF from glucose [9]. Recently, Xia et al. reported one-pot synthesis of HMF from cellulose by using  $\text{FePO}_4$  as a catalyst, in which about 49.5% yield of HMF was obtained [10]. Although higher yields of HMF have been observed by the aforementioned methods the metal chloride and/or phosphate catalysts used possess some disadvantages including virulence, pollution, and separation problems.

Hydrolysis of cellulose using solid acid catalysts has attracted attention because such catalysts are reusable and are not corrosive to equipment. The reactions can also be performed under mild conditions. For using biomass, it is important to investigate the use of solid acid catalysts for lignocellulosic biomass liquefaction. If water is used as a solvent, rather than an organic solvent, there is no environmental burden in the biomass transformation reaction because the biomass itself contains a significant amount of moisture. Several studies have reported that solid acid catalysts are effective for converting cellulose to saccharides [11,12]. Many types of solid acid catalysts have been prepared and used for the conversion of glucose into HMF. Takagaki et al. reported that the combination of a solid acid (Amberlyst-15) and a solid base (hydrotalcite) can catalyze glucose into HMF [13]. Yan et al. reported that sulfated zirconia catalysts can be used to synthesize HMF from glucose [14]. Nakajima et al. reported that niobic acid is an efficient water-tolerant Lewis acid capable of dehydrating glucose into HMF [15]. Nikolla et al. reported that Sn-beta zeolite can catalyze glucose in a biphasic system into HMF [16]. Also, hydrolysis mechanism of glucose and HMF using Amberlyst 70 as a solid catalyst and deactivation via polymerization of various products in hydrolysis were investigated by Hu

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**Scheme 1.** Reaction pathway for the production of HMF from cellulose.

et al. [17]. However, there are few studies for the one-pot synthesis of HMF from biomass using solid acid catalysts.

We previously reported a method for the saccharification of cellulose using solid acid catalysts [12,18]. Lignocellulosic biomass can be transformed to monosaccharides. Simultaneously, HMF was formed as a byproduct. Thus, it is evident that HMF could be formed from biomass using a solid acid catalyst by one-pot synthesis. In the present study, the possibility of the one-pot conversion of cellulose into HMF was investigated. Then, the effects of acid type, acid amount, and pore structure of the solid catalysts were elucidated. In addition, the effects of gaseous hydrogen addition on the liquefaction of cellulose and the metal loading of the catalyst on the formation of HMF were investigated.

## 2. Material and methods

### 2.1. Materials

Commercial microcrystalline cellulose (Sigma-Aldrich Corp.) was used as a model biomass compound. The actual biomass used in the liquefaction was reed pulp, and eucalyptus pulp, which are extracts by using a mixed solvent of benzene and ethanol (4:1) from reed, and eucalyptus, respectively [18]. Based on our analytic results, both pulps contained more than 99% of cellulose [19]. The biomass pulp was dried to constant weight at 105 °C, and crushed under 14 mesh.

### 2.2. Preparation of catalysts

All catalysts were prepared using the conventional successive impregnation method according to the reported procedure [20]. Sulfated zirconia ( $\text{ZrO}_2(\text{SO}_4^{2-})$ ) supplied by Daiichi Kigenso Kagaku Kogyo was crushed and screened to provide 20 mesh–80 mesh and was used as the support for the following impregnation. Zirconia powder (30 g) was impregnated with sulfuric acid ( $0.5 \text{ mol L}^{-1}$ ) for 1 h. The sample was then dried at 60 °C for 18 h in an oven and was calcined at 600 °C for 3 h in an electrical furnace. Pt/ $\text{ZrO}_2(\text{SO}_4^{2-})$  catalyst containing 1 wt.% Pt was prepared using aqueous solutions of  $\text{H}_2\text{PtCl}_6$ . The other three catalysts, Ru/ $\text{ZrO}_2(\text{SO}_4^{2-})$ ,  $\text{CeO}_2/\text{ZrO}_2(\text{SO}_4^{2-})$ , and  $\text{Nb}_2\text{O}_3\text{CeO}_2/\text{ZrO}_2(\text{SO}_4^{2-})$ , were prepared using an aqueous solution of  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ ,  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , and  $\text{NbCl}_5$ , supplied by Kishida Chemical Co., Ltd. After impregnation, the samples were dried at 105 °C for 1 h in air and were then calcined at 400 °C for 3 h in air. Before the reaction, the catalysts were reduced by  $\text{H}_2$  in situ at 400 °C for 3 h at a flow rate of 30 mL/min of  $\text{H}_2$ .

Mesoporous silica SBA-15 and aluminum-substituted mesoporous silica (Al-SBA-15, Al/Si molar ratio: ca. 10) catalysts were prepared according to procedures described in the literature [21].

The  $\text{Zr-SBA-15}/\text{SO}_4^{2-}$  and  $\text{ZrO}_2/\text{SiO}_2/\text{SO}_4^{2-}$  catalysts were prepared using aqueous ethanol solution, and an appropriate amount of  $\text{ZrCl}_2 \cdot 8\text{H}_2\text{O}$  was heated at 60 °C with stirring to generate a clear solution. Then, SBA-15 or  $\text{SiO}_2$  was added with stirring. The samples were dried at 80 °C for 2 h in air and were then calcined at 600 °C for 2.9 h in air. After calcination, the samples were impregnated with aqueous solution of 1.0 M ( $1 \text{ mol} \cdot \text{dm}^{-3}$ ) sulfuric acid for 15 min and were then calcined at 650 °C for 3.3 h in air.

HY (JRCZ-HY 4.8, Si/Al = 4.8) was provided by the reference catalyst of the Catalysis Society of Japan.

### 2.3. Characterization of catalysts

The specific surface areas and pore sizes were analyzed using Belsorp-mini II (Bel Japan Corp., Japan) for the nitrogen adsorption and desorption isotherms. The specific surface areas and pore volumes were calculated using the Brunauer–Emmett–Teller (BET) method.

The concentrations of the Brønsted and Lewis acidic sites on the samples were determined using the FT-IR spectra of adsorbed pyridine; the measurement was performed on an IRPrestige-21 instrument (Shimadzu Corp.). The sample was pressed into a self-supporting wafer ( $10\text{--}15 \text{ mg/cm}^2$ , diameter = 10 mm) and was inserted into a measurement cell with KBr windows that was connected to a vacuum apparatus. The wafer was treated at 500 °C under vacuum for 2 h and was subsequently cooled to room temperature to collect the background spectra. The pyridine adsorption was performed by equilibrating the wafer for 30 min at 100 °C. To calculate the weak acidic sites and the medium and strong acidic sites, the IR spectra for the samples were recorded after degassing for 20 min at 100 °C.

The thermolysis temperature of raw materials was analyzed using thermogravimetry-differential analysis (DTG-60; Shimadzu Corp.).

### 2.4. Liquefaction reaction

A prepared catalyst (0.5 g), distilled water (30 g), and model or actual biomass (1 g) were put into a 120 mL stainless steel autoclave with an agitation speed of 600 rpm (Taiatsu Tech Corp., TVS-N2), as shown in Fig. 1. Then, the autoclave was rapidly heated to various temperatures from 220 °C to 260 °C for ca. 13 to 15 min and was kept at 220 °C to 260 °C for 0, 5, and 30 min, which were the nominal reaction times, under a gaseous hydrogen or a gaseous nitrogen atmosphere with an initial pressure of 1 MPa. The pressure after having reached the reaction temperature was about 2.5 to 2.7 MPa depending on the temperature. The reaction was stopped by cooling the autoclave in an ice water trap. For instance, ‘0 min’ of reaction time means that the autoclave was quickly cooled using ice water trap during ca. 7 min when the temperature at the inside of the reactor reached the desired one. After the reaction, the liquid products were separated from the mixture via filtration using a membrane filter (0.2 μm; Sartorius Stedim Biotech SA, Germany). The mixture of the unreacted cellulose or pulp and the catalyst was washed with distilled water. The unreacted cellulose or pulp was recovered from the suspension solution because the catalyst has a bigger density. Then, the unreacted cellulose or pulp, and the catalyst were dried to a constant weight at 105 °C in an oven, respectively.

### 2.5. Analysis method

After the reaction, the gaseous and liquid products were separated. The conversion of cellulose and biomass was calculated according to Eq. (1). The liquid samples were analyzed using high-performance liquid chromatography (HPLC) equipped with refractive index detectors (LCMS-2020; Shimadzu Corp., Japan). HPLC was used to identify the liquid products in methanol with a TSKgel G-Oligo-PW column (Tosoh Corp., Japan) at 30 °C using  $\text{H}_2\text{O}$  solution as the eluent at a flow rate of 1.0 mL/min. Various organic acids were analyzed using a TSKgel OApak-A column (Tosoh Corp.) at 40 °C using 0.075 M sulfuric acid solution as the eluent at a flow rate of 0.7 mL/min. The yield and selectivity

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