



# Dealuminated Beta zeolite as effective bifunctional catalyst for direct transformation of glucose to 5-hydroxymethylfurfural



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## ABSTRACT

To improve the catalytic performance of Beta zeolite in the direct transformation of glucose into 5-hydroxymethylfurfural (HMF), effects of calcination and steam treatment on the structure of Al atoms in the framework and acid properties of Beta zeolite were examined in detail.  $^{27}\text{Al}$  MAS NMR measurement and IR observation revealed that a part of Si–O–Al bonds in the framework were cleaved to form Al species out of the **BEA** framework during the treatments and these species showed Lewis acidity. Especially, when the ammonium-type Beta was calcined over  $700^\circ\text{C}$  or treated with steam (50 kPa in  $\text{N}_2$  balance) over  $500^\circ\text{C}$ , the amount of Lewis acid sites was increased at the expense of Brønsted acid sites. Thus prepared Beta zeolite catalysts having a sufficient amount of Lewis acid sites were found to be effective bifunctional catalysts in synthesis of HMF from glucose; for example, Beta zeolite prepared by the calcination at  $750^\circ\text{C}$  showed 55% selectivity to HMF at 78% conversion of glucose. We clarified the roles of Lewis and Brønsted acid sites on the Beta zeolite in the direct transformation of glucose to HMF. Furthermore, the reaction mechanism for the isomerization of glucose was investigated by means of isotope experiment using deuterated glucose. Finally, reusability of the Beta zeolite was also investigated.

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## 1. Introduction

Effective utilization of biomass resources into useful materials such as chemicals and fuels has attracted considerable attention as a potential alternative to crude oil [1–4]. Carbohydrates accounts for 75% of annually renewable biomass [5]. Biomass carbohydrates are divided into two types of polysaccharides. One is cellulose, which is a glucose polymer, and the other is hemicellulose, which has some types of polysaccharides containing pentoses, e.g., xylose and arabinose. These carbohydrates can be converted into useful materials through furfural or 5-(hydroxymethyl)-furfural abbreviated as HMF. These compounds have been regarded as a platform material for the production of polymers [6], fine chemicals [7,8] and transportation fuels [9,10]. Increasing attention has been paid to the dehydration of fructose to HMF. Nearly one hundred homogeneous and heterogeneous catalysts have been positively identified as catalysts for the synthesis of HMF from fructose and the promising results have been achieved [11]. Antal et al. conducted the dehydration reaction in sub-critical water containing  $\text{H}_2\text{SO}_4$  to achieve 53% yield of HMF [12]. A biphasic reactor system was reported by Román-Leshkov et al. [13]; in this process, fructose is dehydrated to HMF in HCl aqueous solution containing poly

(1-vinyl-2-pyrrolidinone) or dimethyl sulfoxide. This biphasic system suppresses the undesired side reactions. Furthermore, the produced HMF is continuously extracted into the organic solvent. Moreau et al. studied the dehydration of fructose in the presence of H-mordenite and achieved 73% yield of HMF at 93% conversion of fructose [14].

In contrast, it is much more difficult to transform glucose to HMF, though it would be preferable to develop a process using glucose as feedstock because glucose is the most abundant component of biomass and less expensive than fructose. Since it has been found that fructose is readily dehydrated to HMF, recently, a tandem reaction system combining isomerization of glucose with subsequent dehydration of fructose to HMF has been extensively investigated. In those reports, the combinations of two types of catalysts assisting each step were employed and various types of combinations have been reported so far. Huang et al. achieved 63% yield of HMF by employing glucose isomerase enzyme and HCl aqueous solution containing borate ion as catalysts for the isomerization of glucose and the dehydration of fructose, respectively [15]. Takagaki et al. reported a combination of hydrotalcite and Amberlyst-15 as base and acid catalysts, respectively. In *N,N*-dimethylformamide media, this combination led to 76% selectivity to HMF at 60% of glucose conversion [16].

Water-tolerant Lewis acids that catalyze the isomerization of glucose to fructose even in aqueous media have been reported. It is desirable that the transformation of glucose to HMF is performed

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in water or in mixed solvents containing water because glucose is produced through hydrolysis of glucose polymers such as cellulose and starch. Ishida et al. reported lanthanide chlorides catalyzed the production of HMF from glucose [17]. Heterogeneous Lewis acid catalysts were also reported to be active in the isomerization reaction in water. Recently, Moliner et al. reported that Sn-Beta catalyzed the isomerization of glucose in water at 110–140 °C and the catalyst can be used multiple times [18]. Following this report, the reaction systems pairing Sn-Beta and some types of Brønsted acid catalysts were developed. Nikolla et al. reported the combination of Sn-Beta and HCl acidic solution that gave 57% yield of HMF in a water-THF biphasic system [19]. The combination of Sn-Beta and Amberlyst resins in a monophasic solvent composed of water and THF was found to give excellent results (63% yield of HMF based on glucose) [20]. Although these catalysts showed good performance, the preparation of Sn-Beta generally require cost and time and some special additives are required to achieve a high catalytic performance. The developments of easily available catalysts with higher catalytic performance and a simple reaction system have been desired. Some research groups reported examples of a reaction system using transition metal oxides modified with H<sub>3</sub>PO<sub>4</sub> as “single catalyst” that shows an activity in both isomerization and dehydration in water [21–23].

In the present study, we performed calcination at high temperature or steam treatment on Beta zeolite (<sup>+</sup>BEA-type aluminosilicate zeolite) to induce a type of dealumination, which is a partial cleavage of Si–O–Al bonds in the framework to form Al species out of the framework. We found that Beta zeolites, which have two types of acid sites, are effective bifunctional catalysts in the tandem reaction combining the isomerization of glucose to fructose and the dehydration of fructose to HMF. Lewis acid sites on the zeolites are active in promoting the isomerization through a hydride transfer mechanism as clarified by an isotope experiment using deuterated glucose. On the other hand, their Brønsted acid sites accelerate the subsequent dehydration of fructose to HMF.

## 2. Experimental

### 2.1. Catalyst preparation

The aluminosilicate zeolite with <sup>+</sup>BEA topology was synthesized in the media containing fluoride anion according to the previous report [24]. Tetraethylammonium cation was used as structure-directing agent (SDA) in the synthesis. Aluminum isopropoxide (Kanto chemical) was added to tetraethylammonium hydroxide solution (Alfa aesar) with stirring. Then, tetraethyl orthosilicate (TEOS) purchased from Tokyo Chemical Industries was added and the mixture was stirred until the complete evaporation of ethanol. Finally, HF aq (Wako) was added. The molar composition of the gel was 1.0 TEOS:0.5 TEOH:0.067 Al(O<sup>i</sup>Pr)<sub>3</sub>:8 H<sub>2</sub>O:0.5 HF. Thus obtained thick gel was transferred to a Teflon-lined stainless steel autoclave and crystallized at 140 °C for 5 days with tumbling. The solid product was recovered by filtration, washed with distilled water and dried overnight at 100 °C followed by calcination at 580 °C to remove SDA. This sample is denoted as Beta-SDAcal. The calcined sample was stirred in 1.0 M NH<sub>4</sub>NO<sub>3</sub> solution at 80 °C for ion-exchange. This treatment was repeated two times to obtain an ammonium form, denoted as Beta-NH<sub>4</sub>.

Beta-NH<sub>4</sub> was calcined in air at different temperatures (500–750 °C) to obtain the proton-form samples. Thus prepared samples are designated as Beta-Calx, where x is the calcination temperature. Steam-treatment of ammonium-form samples was also performed at 500–600 °C. The 1 g of the sample packed in a quartz tube was heated to the desired temperature at the rate of 3 °C/min in air flow and then the gas flow was switched to a steam flow

(50 kPa in N<sub>2</sub> balance) at the flow rate of 50 ml/min. After 1 h of the treatment, the steam flow was stopped and the sample was cooled down under nitrogen flow. The steam-treated samples are designated as Beta-STy, where y is the treatment temperature.

### 2.2. Characterization of the prepared catalysts

Powder X-ray diffraction (XRD) patterns of the prepared samples were collected on a Rigaku Ultima III diffractometer using a Cu K $\alpha$  radiation (40 kV, 20 mA). Chemical compositions of the zeolites were analyzed by a Shimadzu ICPE-9000 analyzer. Solid-state <sup>27</sup>Al MAS NMR spectra of hydrated samples were obtained on a JEOL ECA-600 spectrometer at a resonance frequency of 156.4 MHz using a 4 mm sample rotor with a spinning rate of 15 kHz. <sup>29</sup>Si MAS NMR spectra were measured on a JEOL ECA-400 spectrometer at a resonance frequency of 399.0 MHz using a 6 mm sample rotor with a spinning rate of 5.5 kHz.

The catalyst samples were characterized by FT-IR spectroscopy. FT-IR spectra were obtained by a Jasco FT-IR 4100 spectrometer equipped with an MCT detector. For FT-IR observation, a self-supporting disk of each sample was placed in a quartz cell connected to a closed gas-circulation system. After the sample was pretreated at 450 °C *in vacuo*, a spectrum was recorded at 150 °C. Acid properties of the samples were evaluated by using pyridine as probe molecule. After the record of the spectra at 150 °C, an excess amount of pyridine (~1 kPa) was introduced into the cell and the sample was held at that temperature for 15 min. Then the sample was heated to 250 °C and then the cell was evacuated for 10 min to pump off pyridine desorbed from silanol groups and weak acid sites. The sample was cooled to 150 °C and IR spectra were recorded. This process was repeated with the temperature varied ranging from 250 to 450 °C. For quantitative calculation of adsorbed pyridine, the reported molar extinction coefficient was used [25].

### 2.3. Catalytic tests

Catalytic tests were performed in a Teflon-lined stainless-steel autoclave (50 ml). The reaction mixture was heated by a heating jacket outside the autoclave. At a set time, the reaction was quenched by cooling the autoclave in an ice bath. The reaction mixture was filtered prior to quantitative analysis to remove the solid catalyst. For the reaction in a mixed solvent, the homogeneous solution after the filtration was separated into aqueous and organic phases by adding NaCl as salting-out agent. Sugar substrates and water-soluble products in the aqueous phase were analyzed by an HPLC (Shimadzu, LC-20A) with refractive index and UV (280 nm) detectors in the ion-exclusion mode. HMF and furfural in the organic phase were analyzed by another HPLC (Shimadzu LC-10A) with UV detector (260 nm).

<sup>13</sup>C NMR spectra of the collected fractions (shown in Section 3.3.2) were recorded on a JEOL GX500 spectrometer with <sup>1</sup>H broadband decoupling. To a 5 mm sample tube containing the collected aqueous solution was added a capillary tube packed with D<sub>2</sub>O for locking.

## 3. Results and discussion

The as-synthesized sample showed a typical XRD pattern assigned to the <sup>+</sup>BEA-type structure. After the calcination at 580 °C (Beta-SDAcal) followed by the ion-exchange to the ammonium form (Beta-NH<sub>4</sub>), the framework structure was retained (Fig. 1). Fig. 2 shows <sup>27</sup>Al MAS NMR spectra of these three samples. The as-synthesized sample with the Si/Al atomic ratio of 15 gave peaks at around 55 ppm, which are assigned to tetrahedral Al atoms in the framework (Fig. 2(a)). For Beta-SDAcal, a sharp peak was newly observed at 0 ppm, indicating the formation of octahedral Al

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