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Enhanced production of hydroxymethylfurfural from fructose with solid acid catalysts by simple water removal methods

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ABSTRACT

This paper demonstrates two simple ways to increase 5-hydroxymethylfurfural (HMF) yield (selectivity) in fructose dehydration with various solid acid catalysts. One is a water removal from the reaction mixture by a mild evacuation at 0.97×10^5 Pa; it increases HMF yield for various catalysts (heteropoly acid, zeolite, and acidic resin). The removal of water suppresses two undesired reactions: the hydrolysis of HMF to levulinic acid and the reaction of partially dehydrated intermediates to condensation products. The other method is a decrease in the particle (bead) size of the resin (Amberlyst-15). The crushed and sieved Amberlyst-15 powder in a size of 0.15–0.053 mm shows 100% HMF yield at high fructose concentration (50 wt.% in DMSO), which is to our knowledge the highest yield to date. Near-infrared spectroscopic characterization of adsorbed water suggests that the enhanced yield can be caused by an improved removal of adsorbed water in a small-size resin particle.

1. Introduction

Saccharides have attracted much attention as biomass for substituting petroleum resources, and their conversion to useful chemicals has actively been investigated [1–18]. 5-Hydroxymethylfurfural (HMF), which can be prepared by dehydration of saccharides, is known as a starting material in a possible production of biomass-derived fuels as well as a key platform compound for non-petroleum derived chemicals [1–3]. One of its derivatives, 2,5-furandicarboxylic acid, may replace terephthalic acid as a monomer in the preparation of plastics. The most convenient synthetic method of HMF is based on the acid-catalyzed triple dehydration of fructose, and many types of acid catalysts have been used in this process, such as mineral acids [3–6], strong acid cation exchange resins [7–10], and H-form zeolites [11,12]. Heterogeneous acid catalysts [7–16] offer the advantage of a very easy separation from the reaction products and recycle, thus appearing the most suitable catalysts for a potential industrial process. However, the HMF yield in the literature was less than 90%, because of the formation of various byproducts. As shown in Scheme 1 [3,18], the HMF synthesis begins with removal of one or two water molecules from fructose to form partially dehydrated intermediates. A further dehydration of these intermediates leads to the final product (HMF), but inter-molecule reaction of these intermediates leads to a condensation products, such as soluble polymers and insoluble humins [3]. Another possible way of byproduct formation is a hydrolysis (rehydration) of HMF to give levulinic acid. Thus, one expects that removal of water from the reaction mixture promotes further dehydration of partially dehydrated intermediates and suppresses the hydrolysis of HMF, resulting in an increase in the HMF selectivity. Dumesic and coworkers reported a two phase reactor system to separate HMF from the aqueous reaction medium [18]. Using 7:3(8:2 Water:DMSO):PVP mixture as a reaction media and MIBK as a extraction phase, 60% HMF selectivity at 89% fructose conversion of 60% at high fructose concentration (50 wt.%) was achieved with acidic resin catalyst. This value is still not excellent even though the reaction were performed at high reaction temperature (180 °C). In this study we present a simple approach to achieve high HMF production: water removal from the reaction mixture by a continuous mild evacuation. This method is effective for various solid acid catalysts, including heteropoly acid, zeolite, and acidic resins. In addition, during a course of this study we find that decrease in the particle (bead) size of Amberlyst-15 resin improved HMF yield even without evacuation. Combined with a characterization of adsorbed water, the enhanced yield will be explained by an improved removal of adsorbed and near-surface water in a small-size resin particle.

2. Experimental

H-BEA zeolite (JRC-Z-HB25, $SiO_2/Al_2O_3 = 25 \pm 5$) and H–Y zeolite (JRC-Z-HY 4.8, $SiO_2/Al_2O_3 = 4.8$) were supplied from the Catalysis Society of Japan. A Keggin type heteropoly acid, $H_3PW_{12}O_{40} \cdot 28H_2O$, was obtained from Nippon Inorganic Color and Chemicals Co. $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (surface area = 116 $m^2\ g^{-1}$) was prepared by

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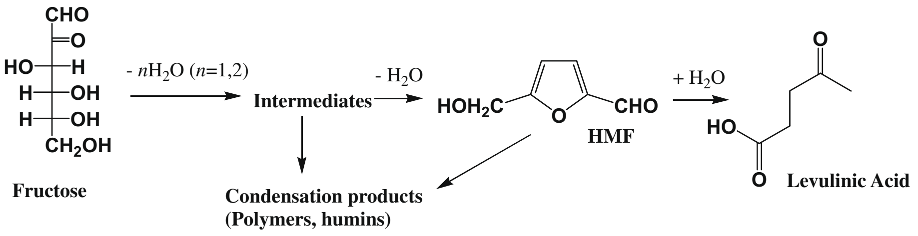

Scheme 1.

titrating $H_3PW_{12}O_{40}$ by cesium carbonate in aqueous solution according to the literature method [19]. Fe(III) salt of $PW_{12}O_{40}^{3-}$ ($FePW_{12}O_{40}$) was prepared by stirring an aqueous solution containing $H_3PW_{12}O_{40}$ and $FeCl_3 \cdot 6H_2O$, followed by evaporation to dryness at 80 °C according to our previous report [20]. Hydrated zirconia was prepared by hydrolysis of zirconium oxynitrate 2-hydrate in distilled water by adding an aqueous NH_4OH solution (1.0 mol dm^{-3}), filtration of precipitate, washing with distilled water for three times, and drying at 100 °C for 24 h in air. WO_3/ZrO_2 was prepared by impregnation of the hydrated zirconia with an aqueous solution of ammonium paratungstate at pH 10 with an aqueous NH_4OH solution, followed by drying at 100 °C and by calcining at 600 °C [21]. Sulfated ZrO_2 (denoted as SO_4^{2-}/ZrO_2) was prepared by mounting H_2SO_4 on the hydrated zirconia, followed by calcination at 600 °C [22]. Amberlyst-15 and Nafion–H were purchased from Aldrich. As received Amberlyst-15 beads (16–50 mesh) were sieved with a stainless mesh (22–30 mesh) to obtain Amberlyst-15 beads with diameter in a range of 0.71–0.50 mm, which was named Amberlyst-15 in this paper. As received Amberlyst-15 beads were crushed and sieved with a stainless mesh (100–282 mesh) to obtain Amberlyst-15 powder with diameter in a range of 0.15–0.053 mm named Amberlyst-15-P in this paper. Amberlyst-15 powder with diameter in a range of 0.20–0.30 mm was also prepared with a stainless mesh (50–74 mesh). These three samples were used to study the effect of particle size.

Diffuse reflectance Near-infrared spectra were measured with JASCO V-570. Thermal gravimetric (TG) analysis was performed with TG/DTA apparatus (TG8120, Rigaku) under N_2 (100 cm^3 min^{-1}) at a constant rate of 10 °C min^{-1}.

D-Fructose (purity: 99%) and dimethyl sulfoxide (DMSO) were purchased from Tokyo Chemical Industry Co., Ltd. DMSO was dehydrated with molecular sieve 3A. Batch catalytic experiments without evacuation were performed under N_2 (ca. 1.01×10^5 Pa) in a tubular glass reactor (100 cm^3). In the reaction under mild evacuation, the upper side of the reactor was equipped with a valve connected to a continuously operated dry vacuum pump (DTC-21, ULVAC), and the pressure during the reaction was typically 0.97×10^5 Pa. A mixture of fructose (0.3 g, 1.7 mmol) and DMSO (10 g) with catalyst powder (0.02 g) was stirred (600 rpm) at 120 °C. The major product, HMF, was identified by GC–MS with Rtx-65TG capillary column. HMF yield was calculated with gas chromatography (Shimadzu GC-14B equipped with FID detector and Rtx-65TG capillary column) using *n*-decane as internal standard. The concentrations of fructose, levulinic acid, and formic acid were analyzed by HPLC using PU-2089 (JASCO) pump equipped with a refractive index detector (RI-2031, JASCO), using a Sugar-Pak Ca column (column temperature 80 °C). Degassed water as the eluent was fed at a flow rate of 0.6 cm^3 min^{-1}. Authentic samples of fructose, levulinic acid, and formic acid were used as standards and calibration curves were used for quantification.

Microcalorimetric measurement on NH_3 adsorption was performed at 150 °C using a calorimeter (Tokyo Rikou Co., HAC-450G) connected to a volumetric glass line (35 °C) with on-line injection system for pulsing NH_3 gas. Before the adsorption experiments the sample (0.1 g) was pretreated under vacuum for 3 h at 150 °C.

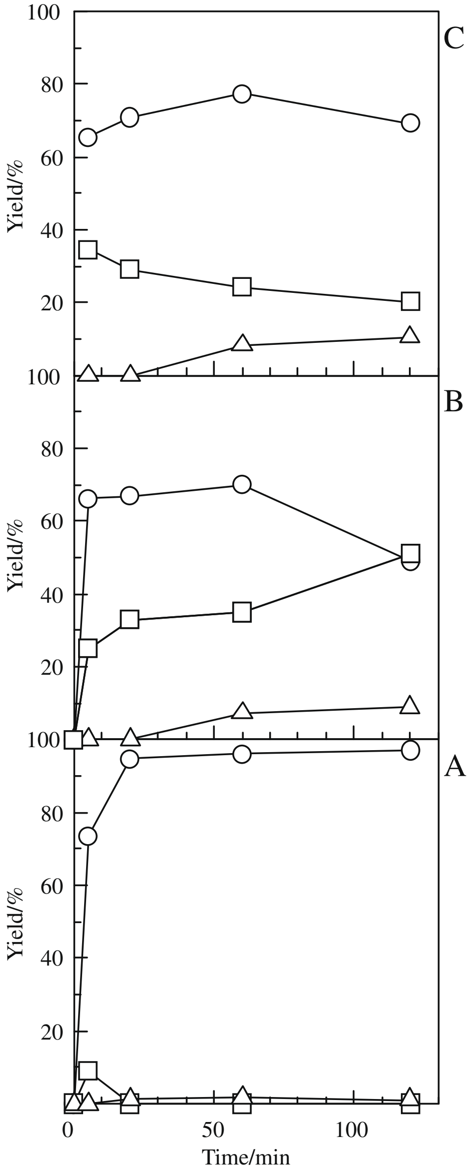

Fig. 1. Yields of (○) HMF, (△) levulinic acid, and (□) non-identified products for fructose (1.7 mmol) dehydration in DMSO (10 g) at 120 °C with $FePW_{12}O_{40}$ catalyst (20 mg) under various conditions: (A) under evacuation ($P = 0.97 \times 10^5$ Pa), (B) without evacuation, and (C) without evacuation with molecular sieves (3 g).