



Short communication

Quantitative synthesis of 2,5-bis(hydroxymethyl)furan from biomass-derived 5-hydroxymethylfurfural and sugars over reusable solid catalysts at low temperatures



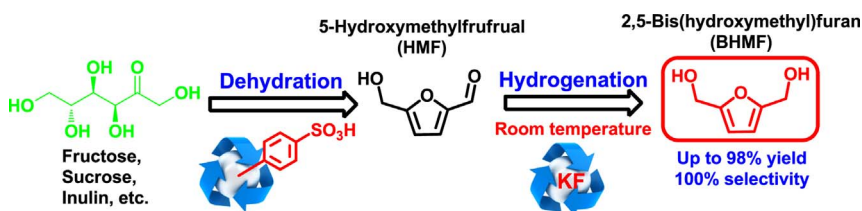
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GRAPHICAL ABSTRACT

Recyclable KF-mediated catalytic system could efficiently promote the quantitative synthesis of 2,5-bis(hydroxymethyl)furan (BHMF) directly from biomass-derived 5-hydroxymethylfurfural (HMF) and sugars using polymethylhydrosiloxane (PMHS) as liquid H-donor under mild conditions at as low as room temperature.



ARTICLE INFO

Keywords:

Biofuels
Biomass conversion
Hydrogenation
Alkali salt
Heterogeneous catalysis

ABSTRACT

Quantitative production of 2,5-bis(hydroxymethyl)furan (BHMF) was achieved at room temperature (25 °C) via highly selective hydrogenation of biomass-derived 5-hydroxymethylfurfural (HMF) employing alkali salt KF as catalyst and polymethylhydrosiloxane (PMHS) as hydrogen source. A moderate turnover frequency (TOF: 4.2 h⁻¹) was observed for this mild and sustainable reaction process. Moreover, a combination of Amberlyst-15 with KF could successfully catalyze the direct synthesis of BHMF from hexose sugars such as fructose and inulin via tandem dehydration and hydrogenation in a single pot. This catalytic system is more selective compared with H₂-participated counterpart, giving a high BHMF yield and selectivity of up to 98% and > 99% from HMF, respectively. Moreover, the catalytic performance of KF could remain for at least five consecutive cycles in the conversion of HMF to BHMF.

1. Introduction

Highly selective production of biofuels and value-added chemicals from biomass derivatives is an essential strategy to achieve the goal of a more sustainable future. Chemocatalytic conversion of bio-based sugars, the most abundant component in lignocellulosic biomass, to

platform molecules has been one of research hotspots for biomass valorization [1,2]. In particular, 5-hydroxymethylfurfural (HMF) dehydrated from sugars (e.g., glucose and fructose) is considered as a multi-purpose compound for further downstream transformations [3]. As one of promising intermediates for diversified essential industry polymerization and etherification processes, 2,5-bis(hydroxymethyl)furan

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(BHMF) can be produced by selective hydrogenation of HMF [4]. Noble metals such as Pt, Pd and Ru have been reported to be capable of hydrogenating HMF to BHMF with moderate yields (ca. 70%) using high pressure H₂ (1–5 MPa) as hydrogen source under harsh reaction conditions [5–7]. Likewise, liquid hydrogen sources (e.g., alcohols and formic acid) were also employed for the reduction of HMF over transition metal catalysts, while those catalytic processes always accompanied by low BHMF selectivities (ca. 70%), high reaction temperatures (> 150 °C) and substantial excess of H-donors [8,9]. Therefore, the development of efficient catalytic systems using equivalent H-donors under mild conditions is highly essential for selective hydrogenation of HMF to BHMF.

Among different types of H-donors, silanes are typically inexpensive, easy to handle, and effective to render H⁻ species under benign conditions [10]. Polymethylhydrosiloxane (PMHS), a castoff generated in the silicon industry, have been widely applied in various reactions such as reduction of amide and carbonyl compounds, and capture of carbon dioxide [11–13]. Typically, the involved hydrosilylation process can take place where the silane is activated by a metal complex, noble metal, *N*-heterocyclic carbene, or metal hydride. However, the above-mentioned catalysts are always too expensive and hard to operate [14].

On account of these enlightenments, we herein report an efficient and facile catalytic system for the production of BHMF using a cheap salt potassium fluoride (KF) as catalyst and PMHS as H-donor at room temperature. To the best of our knowledge, no efficient catalytic systems have been disclosed for the one-pot conversion of HMF and fructose to BHMF. Approximately quantitative yields of BHMF could be obtained from HMF hydrogenation. Furthermore, the synthesis of BHMF from fructose could also be achieved by using Amberlyst-15 as acid catalyst to promote fructose dehydration and KF as co-catalyst to facilitate the hydrogenation of *in situ* formed HMF via a two-step process in a single pot. More importantly, the solid KF catalyst was remarkably stable and remained unchanged catalytic activity in at least five continuous cycles.

2. Materials and methods

2.1. Materials

PMHS, dimethyl sulfoxide (DMSO, > 99.8%), acetonitrile (MeCN, > 99%), tetrahydrofuran (THF, > 99%), *n*-butanol (*n*-BuOH, > 99%), γ -valerolactone (GVL, > 99.8%), 2,5-bis(hydroxymethyl)furan (BHMF, > 99%), and 5-hydroxymethylfurfural (HMF, > 99%) were bought from Shanghai Aladdin Industrial Inc. KF (99%), CsF (99%), LiF (> 99%), NaF (> 99%), KCl (> 99%), KBr (> 99%), RbF (> 99%), and KI (> 99%) were purchased from Beijing Innochem Sci. & Tech. Co. Ltd. Fructose (> 99%), sucrose (> 99%), inulin (> 99%), and Amberlyst-15 (> 99%) were purchased from Beijing J&K Scientific Ltd.

2.2. Catalyst characterization

Scanning transmission electron microscope and high-angle annular dark-field (STEM-HAADF) imaging was acquired with an aberration corrected FEI TECNAI G2 F30 S-TWIN (STEM) (Hillsboro, OR) operating at 300 kV, along with the capability of taking energy dispersive X-ray (EDX) spectra. The elemental contents were determined by ICP-OES (inductively coupled plasma-optical emission spectrometer) on an Optima 5300 DV instrument (PerkinElmer Inc., Waltham).

2.3. Reaction procedure

All the reactions were carried out in 15 mL Ace pressure tube. In a typical procedure of HMF hydrogenation, 0.5 mmol HMF, 10 mg KF,

2.0 mL DMSO and 100 mg PMHS were put into the tube. Then, the mixture was transferred into a temperature-controlled oil-bath and stirred at 500 rpm for a specific reaction time. In the procedure of conversion of sugar to BHMF, 0.5 mmol sugar and 15 mg Amberlyst-15 were first added into the tube loaded with 2.0 mL DMSO. After this mixture reacting for 45 min at 120 °C, Amberlyst-15 was removed through filtration, followed by addition of 10 mg KF and 100 mg PMHS for HMF hydrogenation at room temperature. The zero time was recorded as the pressure tube was overwhelmed into the oil bath preheated at a desired temperature. Upon completion of the reaction and cooling down to room temperature, 10 mg naphthalene was added into the reaction mixture as internal standard. The liquid was filtrated by a 0.2 μ m membrane filter, and BHMF yield was then quantitatively analyzed by GC (Agilent 7890B) and HMF yield and fructose conversion were analyzed by high performance liquid chromatography (HPLC).

2.4. Analysis of products

The concentrations of sugars and HMF were determined by HPLC (LC-20A, Shimadzu, Kyoto) fitted with an Aminex HPX-87H column (Bio-Rad, Richmond, CA) and a refractive index (RI) detector as well as an ultraviolet (UV) detector at 280 nm. The BHMF yield was quantified by GC (Agilent 7890B) with a HP-5 column (30 m \times 0.320 mm \times 0.25 μ m) and a flame ionization detector using naphthalene as internal standard by referring to the standard curves (with R² > 0.999) made from commercial samples. Liquid products and major by-products were identified by GC-MS (Agilent 6890 N GC/5973 MS, Santa Clara, CA).

2.5. Catalyst recycling

After each cycle of reactions, the remaining catalyst in the mixture was recovered by centrifugation, followed by continuously washing with DMF and acetone for 3–5 times, and drying at 80 °C in the atmosphere of N₂ for 6 h, which was then directly applied for the next run.

3. Results and discussion

3.1. Catalyst screening

In our initial experiments, the reduction of HMF was performed with PMHS as hydrogen donor (H-donor) in the presence of various alkali metal catalysts (i.e., KF, CsF, LiF, NaF, KCl, RbF, KI and KBr). It was observed that fluorine salts of potassium, rubidium and caesium at room temperature (25 °C) after 6 h in DMSO could catalyze the complete hydrogenation of HMF (> 99% conversion) to BHMF with yields of 95%, 97% and 99%, respectively (Table S1). In sharp contrast, the other salts such as LiF, NaF, KCl, KBr and KI did not show any reactivity for HMF hydrogenation. These findings indicated that the type of anions correlated with alkali metal species had a synergistic effect on the catalytic activity. Our results are consistent with previous reports [15–16], where fluoride anion (F⁻) serves as a very powerful nucleophilic reagent that can activate silane to supply H⁻ for HMF hydrogenation. Moreover, the effect of different solvents on the conversion of HMF to BHMF was also investigated in the presence of KF (Table S2). It was observed that other organic solvents including acetonitrile (MeCN), *n*-butanol (*n*-BuOH), tetrahydrofuran (THF) and γ -valerolactone (GVL) manifested relatively low performance with respect to HMF conversion and BHMF yield/selectivity (Table S2), as well as high solubility toward KF. In sharp contrast, DMSO has been reported to have capacity to promote both fructose dehydration and HMF hydrogenation [17], while can not dissolve KF (0.008 wt% solubility in DMSO) [18]. Therefore, KF was selected as optimal catalyst for subsequent studies, taking into account of its low solubility in DMSO, high stability, and low-cost.

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