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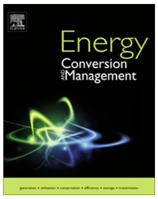

Direct catalytic transformation of carbohydrates into 5-ethoxymethylfurfural with acid–base bifunctional hybrid nanospheres

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ABSTRACT

A series of acid–base bifunctional hybrid nanospheres prepared from the self-assembly of basic amino acids and phosphotungstic acid (HPA) with different molar ratios were employed as efficient and recyclable catalysts for synthesis of liquid biofuel 5-ethoxymethylfurfural (EMF) from various carbohydrates. A high EMF yield of 76.6%, 58.5%, 42.4%, and 36.5% could be achieved, when fructose, inulin, sorbose, and sucrose were used as starting materials, respectively. Although, the acid–base bifunctional nanocatalysts were inert for synthesis of EMF from glucose based carbohydrates, ethyl glucopyranoside in good yields could be obtained from glucose in ethanol. Moreover, the nanocatalyst functionalized with acid and basic sites was able to be reused several times with no significant loss in catalytic activity.

1. Introduction

Selective transformation of biomass resources into fuels and chemicals with efficient catalysts is one of the major challenges facing the chemical industry [1–7]. Over the past decades, furanic derived products, such as 5-hydroxymethylfurfural (HMF), furfural, 2,5-furandicarboxylic acid, 2,5-diformylfuran, 2,5-bishydroxymethylfuran, and 2,5-dimethylfuran, have received wide attention and showed great potential in the replacement of fuels and chemicals currently produced from fossil resources [8]. Amongst, 5-ethoxymethylfurfural (EMF) with a high energy density of 30.3 MJ L^{-1}, close to that of diesel (33.6 MJ L^{-1}) and ethanol (23.5 MJ L^{-1}), is thereby proposed to be one of potential liquid biofuels [9].

Various acidic catalysts including metal chlorides, mineral acids, and solid acids have been employed for synthesis of EMF from HMF or carbohydrates. Starting from HMF, Che et al. [10] illustrated that $H_4SiW_{12}O_{40}$/MCM-41 nanospheres were efficient for production of EMF with selectivity of 84.1% at HMF conversion of 92.0%. In contrast to Brønsted acids, solid catalysts with strong Lewis acid sites (e.g., introduction of ZrO_2 into SBA-15 or presence of extra-framework isolated Al^{3+} sites in MCM-41) could afford a higher yield to EMF (up to 76%) with HMF conversion of 100% at 140 °C for 5 h [11]. With respect to one-pot catalytic conversion of carbohydrates into EMF, reaction systems containing $AlCl_3$, $FeCl_3$, NH_4Cl or $H_3PW_{12}O_{40}$ (HPA) were capable of successively catalyzing dehydration of fructose to HMF and etherification of HMF with ethanol to EMF [12–18].

From an economical and environmental point of view, catalytic sequential dehydration–etherification of carbohydrates into EMF with heterogeneous catalysts was required to be developed. As such, silica coated magnetic Fe_3O_4 nanoparticles and K-10 clay supported phosphotungstic acid were demonstrated to be efficient for the synthesis of EMF from fructose, giving a maximum EMF yield of 54.8% and 61.5%, respectively [19,20]. Simultaneously, sulfonic acid functionalized catalysts were also illustrated to exhibit efficient catalytic performance for selective conversion of fructose into EMF. Kraus and Guney [21] found that SO_3H-functionalized ionic liquids together with hexane resulted in a 54% isolated yield from fructose at 100 °C for 80 min. Using silica supported sulfonic acid as a heterogeneous catalyst, EMF could be obtained in a high yield of 63.1% from fructose at 100 °C for 24 h [22]. A cellulose sulfuric acid could be used as an efficient and environmentally friendly bio-supported catalyst for the synthesis of EMF from fructose, giving a EMF yield of 72.5% through

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one-pot reaction at 100 °C within 12 h [23]. A high EMF yield of 90.5% could be obtained from fructose with the presence of methylimidazolebutylsulfate phosphotungstate ($[MIMBS]_3PW_{12}O_{40}$) at 90 °C for 24 h [24]. Two different types of solid acid catalysts (i.e., Brønsted acid Amberlyst 131 and Lewis acid zeolite Sn-BEA) were synergistically employed for conversion of glucose to EMF, and a moderate yield of EMF (31%) could be achieved in ethanol in a single reactor at 90 °C after 24 h [25].

As described above, direct catalytic conversion of carbohydrates into EMF can proceed in the presence of both homogeneous and heterogeneous catalysts with Brønsted acidic sites and/or Lewis acidic sites. However, relatively low yields of EMF are always observed, which may be ascribed to the lack of highly efficient catalytic sites in selective etherification of HMF with ethanol as well as the low stability of EMF that can be further converted into ethyl levulinate. In this regard, new catalytic systems with good reactivity and suitable acidity or basicity need to be developed for the sequential reaction. Interestingly, the catalytic activity of etherification could be controlled by both the surface basicity for deprotonation of alcohol and Lewis acidity facilitating the elimination of the OH group from the counterpart [26–28]. On the other hand, isomerization of glucose into fructose could be catalyzed by solid base and dehydration of fructose into HMF which might be further converted into EMF in ethanol by solid acid (Scheme 1) [29,30]. Nevertheless, the liquid acid–base pair can never be adopted in one pot because of their neutralization. Consequently, to prepare acid–base bifunctional catalysts with heterogeneous behavior would be helpful for one-pot sequential catalysis which might involve hydrolysis, isomerization, dehydration, and etherification reactions.

In the present study, a series of nanocatalysts functionalized with both acidic and basic sites were synthesised from self-assemble of corresponding basic amino acids with phosphotungstic acid (HPA). It was demonstrated that these amphiphilic catalysts not only highly promoted the sequential dehydration–etherification reaction, but also played a certain role in isomerization and even hydrolysis reaction. Apart from reaction conditions as reaction temperature and time, the distribution of acid–base sites in these amphiphilic catalysts was demonstrated to be another main factor on determining the yields of EMF as well as ethyl D-glucopyranoside.

2. Experimental

2.1. Materials

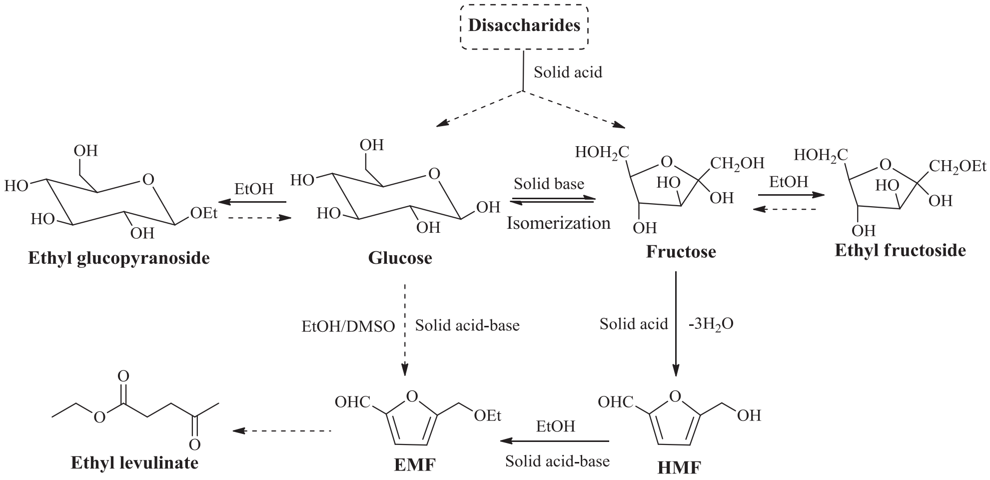
Fructose (99%), sorbose (⩾98%), glucose (⩾99.5%), inulin (from dahlia tubers), cellobiose (99%), 5-ethoxymethylfurfural (97%), lysine (⩾98%), arginine (⩾98%), histidine (⩾98%), HCl (37%), and phosphotungstic acid hydrate (HPA, reagent grade) were purchased from Sigma–Aldrich. 5-Hydroxymethylfurfural (>99%) was purchased from SAFC, ethanol (99.9%) from Kemetyl and sucrose (99%) from Alfa Aesar, and all used without further purification.

2.2. Catalyst preparation

The acid–base nanocatalysts were prepared according to the reported procedures [31] with slight modification. To a solution containing an amino acid (2 mmol) dissolved in dilute hydrochloric acid (1 mol L^{-1}, 5 mL), $H_3PW_{12}O_{40}$ (HPA) (1 mmol) in dilute hydrochloric acid (1 mol L^{-1}, 5 mL) was slowly added. The resulting mixture was stirred at room temperature, and the precipitates were obtained by continuously stirring over night, and then filtered, washed with water and dried at 60 °C for 4 h to give the acid–base nanocatalysts with amino acid/HPA molar ratio of 2 as a white solid. The acid–base nanocatalysts with amino acid/HPA molar ratio of 1 were synthesised with the same method. The catalyst prepared from self-assembly of HPA with lysine, arginine, or histidine having different molar ratios of amino acid to HPA was denoted as Lys/PW(2), Lys/PW(1), Arg/PW(2), Arg/PW(1), His/PW(2), and His/PW(1), respectively.

2.3. Catalyst characterization

FTIR spectra of the samples were recorded on a Perkin-Elmer 1710 spectrometer at ambient conditions in KBr disks. X-ray powder diffraction (XRPD) patterns were performed using a Huber G670 powder diffractometer (Cu Kα radiation, $\lambda = 1.54056$ nm) in the 2θ interval 3–60°. Thermogravimetry (TG) analysis was carried out with TGA/DSC 1 apparatus (Mettler Toledo) in the range of 40–600 °C with a heating ramp of 20 °C/min. BET (Brunauer–Emmett–Teller) surface areas of the samples were determined from nitrogen physisorption measurements at liquid nitrogen temperature on a Micromeritics ASAP 2010 instrument. Transmission electron microscopy (TEM) image was acquired using a FEI Tecnai Transmission Electron Microscope operated at 200 kV by dispersing samples on a lacy amorphous carbon support film. The acid capacity of the catalysts was measured by titration with diluted NaOH, and phenolphthalein was used as the indicator [32,33]. The basic capacity was measured by the conductometry [31]. The Hammett acid strength as well as Hammett base strength was measured by exposing samples to benzene solutions of a known amount of selected Hammett indicators.



Scheme 1. Proposed reaction pathway for catalytic conversion of carbohydrates into EMF and other products with solid acid–base bifunctional catalyst.