



Magnetically separable base catalysts for isomerization of glucose to fructose



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ABSTRACT

Isomerization of glucose to fructose is a key intermediate step for the biochemical conversion of lignocellulose to liquid fuels and chemicals through the sugar platform. This study demonstrates facile and general strategies to fabricate heterogeneous or magnetic base catalysts based on organic bases for the isomerization of glucose to fructose in water. The heterogeneous or magnetic base catalyst can achieve similar glucose-to-fructose yield and selectivity to homogenous organic base catalyst. The accumulated by-products influence the reusability of the heterogeneous base catalyst; however, the magnetic base catalyst shows excellent stability and reusability.

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1. Introduction

Fructose is the sweetest of naturally occurring sugars and is used commercially in food and beverage. Recently, fructose has been considered as a renewable resource for the production of a versatile platform chemical-5-hydroxymethylfurfural, which can be converted into a number of value-added chemicals, and can be updated into liquid fuels [1–3]. Therefore, isomerization of glucose to fructose is a key intermediate step for the biochemical conversion of lignocellulose to liquid fuels and chemicals through the sugar platform. To date, many efforts have been made to develop catalysts for isomerization of glucose to fructose. Enzymes (i.e. glucose isomerases) have been widely tested as the most effective and selective catalyst for the isomerization of glucose to fructose in aqueous medium. However, the enzymatic isomerization of glucose still faces several drawbacks including high cost of the enzyme, longer reaction time, use of buffering solutions, and irreversible deactivation [4–6]. Lewis acids such as chromium chloride and Sn-beta zeolite have been reported to be effective catalysts for the isomerization of glucose [7–10]. However, the homogenous Lewis acids generally have the issues of separation and recycle, and the synthesis for Sn-beta zeolite is relatively complex. On the other hand, Brønsted bases such as sodium hydroxide can also effectively isomerize the glucose to fructose. However, they typically achieve lower glucose-to-fructose yields due to

severe degradation of fructose and glucose, and they also face the issues of separation and recycle. Metallosilicates have been reported as solid base catalysts for the aqueous phase isomerization of glucose [11]. However, most metallosilicates are prone to be deactivated due to loss of crystallinity, metal iron leaching, and surface passivation. Some metal oxides such as zirconium carbonate, zirconium dioxide, titanium dioxide, and magnesium–aluminum hydrotalcites are effective catalysts under severe reaction conditions (larger loading, longer reaction time and higher temperature) [12–14]. Organic bases such as trimethylamine have been recently identified as highly efficient catalysts in wide range of temperature with the same performance as state of the art Lewis acid catalysts for the aqueous phase isomerization of glucose [15]. However, the facile separation and recycle of organic base are still challenging. Herein, in this study, we developed highly efficient and readily recyclable heterogeneous catalysts based on organic bases for the isomerization of glucose to fructose in water.

2. Experimental

2.1. Materials

Merrifield's peptide resin (PS, chloromethylated polystyrene, 3.5–4.5 mmol/g Cl, 1% cross-linked, 200–400 mesh), imidazole (IMD), N-[2-[bis(2-aminoethyl)amino]ethyl]aminomethyl-poly styrene (PS-TREN, 3.5–5.0 mmol/g N, 1% cross-linked with divinylbenzene), branched polyethylenimine (PEI, $M_n = 1 \times 10^4$), 1-(3-aminopropyl) imidazole (API), tetramethylguanidine (TMG),

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1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), tris(2-aminoethyl)amine (TREN), triethylamine (TEA), chromium chloride hexahydrate ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$), iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), iron (II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), polyvinylpyrrolidone (PVP, $M_w = 4 \times 10^4$), ammonium hydroxide (28–30% NH_3), tetraethyl orthosilicate (TEOS), (3-chloropropyl)trimethoxysilane (CPTS), DL-glyceraldehyde, glycerol, D-fructose, D-glucose and D-deuterated glucose (glucose-2-D) were bought from Sigma–Aldrich. N,N-Dimethylformamide (DMF), sodium carbonate (Na_2CO_3), and ethanol were obtained from Fisher Scientific. All chemicals were used as received.

2.2. Synthesis of heterogeneous base catalyst

Heterogeneous base catalyst was synthesized through the reaction between benzyl chloride in polystyrene resin and organic base (Scheme 1). Briefly, Merrifield's peptide resin (6 g), organic base (80 mmol, API or TMG or TBD), Na_2CO_3 (10 mmol), and DMF (50 mL) were successively added into a 100 mL round-bottomed flask. The mixture was reacted at 80 °C for two days under magnetic stirring. Then, the resultant solid was collected by filtration, intensively washed with water and DMF, and was dried under vacuum.

2.3. Synthesis of silicon dioxide-coated magnetic iron oxide

Magnetic iron oxide (Fe_3O_4) nanoparticles were prepared through a co-precipitation method. Briefly, the mixture of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (81.4 mmol) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (40.7 mmol) in deionized water (120 mL) was heated to 85 °C, and pH value of the mixture was adjusted to 9 by concentrated ammonium hydroxide (28–30% NH_3). Then, the mixture reacted at 85 °C for 4 h under nitrogen protection. The black precipitate was collected and washed to pH = 7 by deionized water. The sediment was redispersed in deionized water (100 mL) containing PVP (0.3 g) under sonication. After stirring for overnight at room temperature, the PVP-stabilized magnetic particles were separated and rinsed by ethanol twice, and were dried under vacuum.

Silicon dioxide-coated magnetic iron oxide was obtained through a modified Stöber process. Briefly, the mixture of magnetic iron oxide particle (20 g), concentrated ammonium hydroxide (20 mL), TEOS (20 mL), and ethanol (400 mL) was stirred for 24 h. Then, the silicon dioxide-coated magnetic iron oxide particles were separated, washed with ethanol for three times, and were dried under vacuum.

2.4. Synthesis of magnetic base catalyst

CPTS (100 mmol) was added to the suspension of silicon dioxide-coated magnetic iron oxide particle (10 g) in toluene (120 mL). The mixture was refluxed for 48 h at 110 °C, and then cooled to room temperature. The functionalized magnetic iron oxide particles with chloride groups were separated by a magnet and washed with ethanol for three times, and were dried under vacuum.

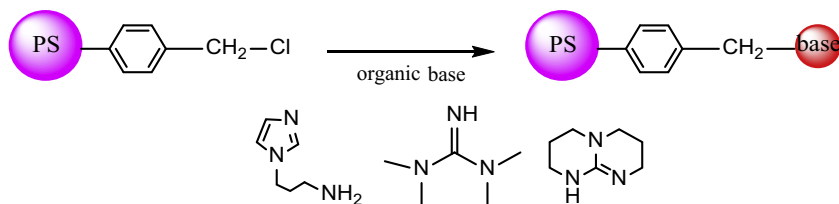
Magnetic base catalyst was then synthesized through the reaction between the chloride group on the surface of the functionalized magnetic iron oxide particle and organic base (Scheme 2). Briefly, the functionalized magnetic iron oxide particles with chloride groups (3 g), organic base (40 mmol, API or TMG or TBD), and Na_2CO_3 (5 mmol) were added into DMF (60 mL). The resulting mixture was refluxed at 85 °C overnight, and the synthesized magnetic base catalyst was separated and thoroughly rinsed with ethanol, and was dried under vacuum.

2.5. Isomerization of glucose to fructose

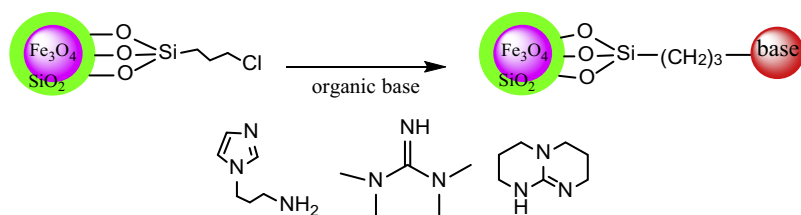
Isomerization experiments of glucose (10% or 20%, wt/wt) in water were carried out in 6 mL thick-walled glass reactors at different temperatures (80, 100 and 120 °C). The isomerization experiment was allowed to proceed for specific times, and then was stopped by cooling the reactor in an ice bath. Small aliquots of the filtered and diluted reaction media were taken for sugar (fructose and glucose) analysis by a high performance liquid chromatography (HPLC).

2.6. Characterization and analysis method

Nitrogen content of base catalyst was determined on a PerkinElmer 2400 Series II Elemental Analyzer 2400. Scanning electron microscopy image was taken using a Hitachi S-900 field-emission scanning electron microscope (SEM) operated at an accelerating voltage of 9 kV. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectrum was recorded on a PerkinElmer Spectrum 100 Series FT-IR spectrophotometer with a universal ATR sampling accessory. Average particle sizes were determined by dynamic light scattering method with a Zeta-sizer Nano ZS instrument equipped with a 633 nm laser. ^1H , ^{13}C NMR and heteronuclear single-quantum correlation (HSQC) spectra were collected with a Bruker Biospin AVANCE 500 MHz NMR



Scheme 1. Synthetic route of the heterogeneous base catalyst.



Scheme 2. Synthetic route of the magnetic base catalyst.

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