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Article

Comparison of cellobiose and glucose transformation to ethylene glycol

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ABSTRACT

Cellobiose was used as a model feedstock to probe the reaction pathways of cellulose to ethylene glycol (EG). Its reactivity was compared with that of glucose using a catalyst composed of H_2WO_4 and Ru/C. EG can be produced by both the direct retro-aldol condensation of cellobiose and the retro-aldol condensation of glucose derived from cellobiose hydrolysis. The direct retro-aldol condensation of cellobiose further promoted the hydrolysis of cellobiose. Cellobiose has a lower reactivity for retro-aldol condensation than glucose, which decreased the formation rate of glycolaldehyde and made it more matched with the subsequent hydrogenation rate, thus leading to increased yield of EG from cellobiose.

1. Introduction

Lignocellulose is the most abundant non-edible biomass in nature, and can be a renewable hydrocarbon source for the production of liquid fuels and chemicals, which is important for a sustainable society [1–22]. Among the various chemical transformation routes of cellulose, the one-pot catalytic transformation of cellulose and hemicellulose to ethylene glycol (EG) and propylene glycol (PG) has attracted considerable attention from both academic and industrial communities because both EG and PG are commodity chemicals widely applied in the polyester industry [22–36]. Since the first report by our group on cellulose conversion to EG [23], much progress has been made in catalyst design and mechanistic understanding both from our groups [24–31] and other groups [21,36]. The original Ni-W_2C/AC catalyst has now been replaced by a more durable and versatile dual component catalyst composed of tungstic acid and Ru/C [30] or Raney Ni [31], which resulted in the significant increase in recyclable times from less than 3 to more than 30. On the other hand, the understanding of the reaction mechanism is approaching knowledge of the nature of the active sites. In particular, the interplay between the tungstic compound and cellulose is now believed to be by homogeneous catalysis instead of heterogeneous catalysis and the selective C-C cleavage of cellulose or glucose follows a retro-aldol condensation pathway [30–35].

In spite of these advances, the elucidation of the reaction mechanism on the molecular level has not been attained yet. For example, the production of EG from cellulose is believed to involve three consecutive reactions: (1) hydrolysis of cellulose to glucose, (2) retro-aldol condensation of glucose to glycolaldehyde (GA), and (3) hydrogenation of GA to EG. However, it is

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known that the hydrolysis of cellulose to glucose proceeds very slowly and many soluble celloligosaccharides are formed as intermediates during the hydrolysis [37,38]. In this case, it will be interesting to know whether these celloligosaccharide intermediates also undergo retro-aldol condensation to produce GA as glucose does, and if they do, to what extent do these reactions contribute to the total production of EG from cellulose.

To address these questions, we made a comparative study of cellobiose and glucose conversion in the present work. Cellobiose is a glucose dimer connected with a β-1,4-glycosidic bond. It is the simplest molecule that resembles the cellulose structure [39–42]. When cellobiose is used as the feedstock, almost all the intermediates can be identified and quantified, which overcomes the difficulty in identifying the intermediates in cellulose conversion. Furthermore, cellobiose has one β-1,4-glycosidic bond and therefore all the reactions that occur on cellulose, namely, hydrolysis, C–C bond cleavage, and hydrogenation, also occur on cellobiose. Therefore, cellobiose is an ideal probe molecule for the mechanistic study of cellulose conversion.

2. Experimental

In all experiments, tungstic acid (H_2WO_4, Sinopharm Chemical Reagent Co., Ltd.), cellobiose (J & K Chemical) and glucose (J & K Chemical) were used as received. Catalytic reactions of glucose and cellobiose were performed in a semi-continuous stainless steel autoclave (Parr Instrument Company, 300 mL) equipped with sampling tube, stirring impeller, and temperature and pressure control systems. In a typical reaction, 0.1 g H_2WO_4, 0.3 g Ru/C, and 90 mL water were put into the autoclave. The autoclave was flushed with H_2 for five times and then sealed. The autoclave was then heated to the desired temperature, and 10 mL of an aqueous solution of glucose or cellobiose at a concentration of 1.63 mol_{carbon}/L was fed in by a Shimadzu LC pump (LC-20A) at a flow rate of 10 mL/min. It took 1 min to finish the feeding process. Then, pure H_2 gas was charged in until a pressure of 6 MPa, and the reaction was started by strong agitation at 1000 r/min, and this point was considered as the initial time (t = 0). Samples were taken from the reactor at fixed time intervals for analysis.

After filtration through a 0.45 μm PTFE filter, the liquid samples were analyzed by a high performance liquid chromatograph (HPLC, Aglient 1200) in combination with mass spectroscopy (MS), with water as the mobile phase and RI as the detector. For the separation of polyols, a Shodex SC100 column was used with a water flow rate of 0.6 mL/min and column temperature of 348 K. For the separation of unsaturated intermediates, a CARBOSep CHO-620 column was used with a water flow rate of 0.4 mL/min and column temperature of 348 K. The qualitative analysis of the intermediates and products was made by HPLC-MS. The quantitative analysis was by an external standard method. The yields of intermediates and products were calculated as: yield (%) = (mass of intermediates or products)/(mass of sugar put into the reactor) × 100%.

The Gibbs free energy of the reactions was calculated with a full electron density functional theory (DFT) calculation by the program package DMol³ in the Materials Studio of Accelrys Inc. [43,44]. Localized double-numerical basis sets with polarization functions (DNP) were used, which are more accurate than but comparable in size to the Gaussian basis sets 6-31G**. The non-local exchange-correlation functional of BLYP was employed. The convergences of energy and gradient used 1×10^{-5} hartree and 2×10^{-3} hartree/Å, respectively.

3. Results and discussion

3.1. Reaction pathway

To understand the reaction pathways for the conversion of cellobiose to ethylene glycol, liquid samples were taken from the reactor at fixed time intervals for analysis. Fig. 1 presents the typical HPLC chromatograph of the liquid products from cellobiose conversion catalyzed by H_2WO_4 and Ru/C at 453 K for 20 min. At least 15 compounds were present in the process of cellobiose conversion and of these, 14 compounds were identified. Among these, glucosyl-erythrose (GE) and glucosyl-erythritol (GER) were particularly interesting because they came from the direct C–C bond cleavage of cellobiose and not glucose by a retro-aldol reaction pathway. The formation of GE in cellobiose conversion was also observed by Arai group under sub- and super-critical water conditions [39,40]. The formation of GER resulted from the hydrogenation of GE over Ru/C, similarly to the formation of 3-β-D-glucopyranosyl-D-glucitol from cellobiose hydrogenation [41,42]. In addition to the C10 and C12 sugar and sugar alcohols, there were also C2–C6 sugars (GA, glucose, mannose, and fructose), sugar alcohols (sorbitol, mannitol, and erythritol), and polyols (EG, hydroxyacetone). In cellulose conversion to EG, most workers believe that cellulose is first hydrolyzed to glucose and the resultant glucose undergoes retro-aldol condensation to produce GA. However, in the present work, the detection of GE and GER unequivocally indicated that GA can also be produced directly from the retro-aldol condensation of cellobiose. By extrapolating this result to cellulose conversion, we concluded that glu-

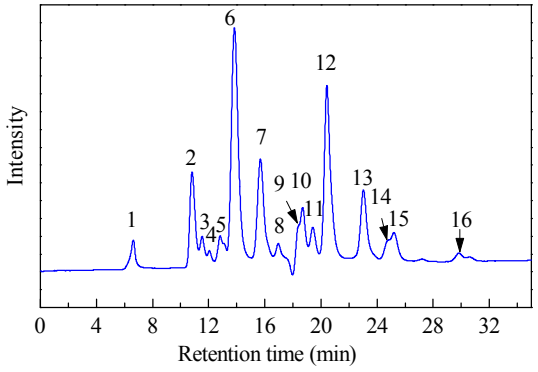

Fig. 1. Typical HPLC analysis for the products of cellobiose conversion catalyzed by H_2WO_4 and Ru/C. Reaction conditions: 0.10 g H_2WO_4, 0.30 g Ru/AC, 453 K, 6 MPa H_2, 20 min, 1000 r/min. 1—Acids; 2—Cellobiose; 3—Glucosyl-erythrose; 4—Glucosyl-erythritol; 5—Glucopyranosyl-D-glucitol; 6—Glucose; 7—Mannose; 8—Fructose; 9—Erythritol; 10—Glycolaldehyde; 11—Mannitol; 12—Ethylene glycol; 13—Sorbitol; 14—Hydroxyacetone; 15—Unknown.