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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.

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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 The original Ni-W₂C/AC catalyst has now been replaced by a more durable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, Agilent 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) $\times$ 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/ $\text{\AA}$, 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/C, 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.

Scheme 1. Primary reaction network for cellobiose conversion catalyzed by H_2WO_4 and Ru/C .

cose would not be the only intermediate sugar during cellulose conversion to EG: other soluble celloligosaccharides derived from the partial hydrolysis of cellulose can also undergo C–C bond cleavage to form GA. Therefore, from the product distribution, we propose the reaction pathway illustrated in Schemes 1–4. The primary reactions (Scheme 1) are three parallel reactions occurring simultaneously: (1) hydrolysis of cellobiose to form two molecules of glucose, (2) retro-aldol condensation of cellobiose to form equal-molar GE and GA, and (3) hydrogenation of cellobiose to 3-β-D-glucopyranosyl-D-glucitol. Then, the products from the primary reactions undergo secondary reactions. In the secondary reactions, glucose, GE, and 3-β-D-glucopyranosyl-D-glucitol further undergo the several parallel and consecutive reactions shown in Schemes 2–4. Clearly, even with the simplest unit of cellulose containing only one β-1,4-glycosidic bond, the reaction network is rather complex, so this will pose a significant challenge for selectivity control for desired products.

On the other hand, from comparing the structure of cellobiose, GE and glycosyl-glycolaldehyde (GG), one can clearly see that the accessibility to the β-1,4-glycosidic bond follows the order $\text{GG} > \text{GE} > \text{cellobiose}$, which suggested that the retro-aldol condensation of aldose at the reducing end will further promote the hydrolysis of the β-1,4-glycosidic bond. The DFT calculation of the Gibbs free energies for the hydrolysis of these three aldoses confirmed our expectation, as shown in Table 1.

3.2. Comparison of glucose and cellobiose transformation

Scheme 2. Reaction network of glucosyl-erythrose catalyzed by H_2WO_4 and Ru/C .

Scheme 3. Reaction network of 3-β-D-glucopyranosyl-D-glucitol catalyzed by H_2WO_4 and Ru/C .

Glucose is the basic unit of cellulose and it is formed as an intermediate in cellulose conversion to EG, while cellobiose is the smallest molecule possessing a β-1,4-glycosidic bond. Cellobiose can be considered to represent soluble celloligosaccharides that are also formed as intermediates during cellulose conversion to EG. Therefore, the comparison of glucose and cellobiose reactivity will provide mechanistic information for the cellulose conversion to EG. First, we conducted reactions at a relatively low temperature (393 K) for 2 h with a dual component catalyst of H_2WO_4 and 1% Ru/C . As shown in Table 2, both the conversion and product distribution were different when the feedstock was changed from glucose to cellobiose. At this low temperature, the cellobiose conversion was only 6.0% while the glucose conversion reached 11.1%, indicating that the intrinsic reactivity of cellobiose was low due to the presence of the β-1,4-glycosidic bond. In the case of cellobiose, 3-β-D-glucopyranosyl-D-glucitol was the major product resulting from the direct hydrogenation of cellobiose. The production of a very small amount of sorbitol (0.16%) suggested that hydrogenation predominated over the hydrolysis of cellobiose at temperatures lower than 393 K. Similarly, hydrogenation also occurred with glucose to produce sorbitol (9.74%) and mannitol (0.08%). No C–C bond cleavage took place at 393 K. Ac-

Scheme 4. Reaction network of glucose catalyzed by H_2WO_4 and Ru/C .

Table 1

Gibbs free energy for the hydrolysis of cellobiose, glucosyl-erythrose (GE), and glycosyl-glycolaldehyde (GG).

Reaction	ΔG (kcal/mol)
Cellobiose+ H_2O →2Glucose	5.276
GE+ H_2O →Glucose+Erythrose	−0.805
GG+ H_2O →Glucose+GA	−0.981

cording to our kinetic studies [45,46], C–C bond cleavage of glucose requires an activation energy of 141.3 kJ/mol while the hydrogenation reaction has a much lower barrier (49.6 kJ/mol). It should also be pointed out that the presence of H_2WO_4 in the reaction system suppressed the hydrogenation of both cellobiose and glucose leading to their low conversion even after 2 h for the reaction at 393 K.

Subsequently, we investigated the reactivities of cellobiose and glucose at higher temperatures from 418 to 513 K. Fig. 2 illustrates the product distributions from cellobiose conversion at four different temperatures. When the reaction of cellobiose proceeded at 418 K, the main products in the initial 240 min were 3- β -D-glucopyranosyl-D-glucitol and glucose, while the other two minor products were sorbitol and EG, indicating that the direct hydrogenation and hydrolysis of cellobiose dominated although the C–C bond cleavage reaction had occurred to a small extent at this temperature. However, with increasing reaction time, both sorbitol and EG increased in their yields at the expense of both 3- β -D-glucopyranosyl-D-glucitol and glucose. When the cellobiose was converted completely at 840 min, the 3- β -D-glucopyranosyl-D-glucitol amount was almost negligible while the sorbitol and EG yields were 42.8% and 21.7%, respectively. The sorbitol came from the hydrolysis of cellobiose as well

as of 3- β -D-glucopyranosyl-D-glucitol followed by the hydrogenation of glucose, while the EG resulted from the retro-aldol condensation of both cellobiose and glucose followed by the hydrogenation of glycolaldehyde, as shown in Schemes 1 to 4.

When the cellobiose reaction was performed at higher temperatures (433–473 K), the reaction rate was remarkably enhanced. For example, cellobiose was completely converted for 360, 50, and 15 min at the reaction temperature of 433, 453, and 473 K, respectively. At the same time, the product distribution changed with increasing temperature. EG rather than sorbitol became the main product at $T \geq 433$ K, indicating the C–C bond cleavage reaction prevailed over hydrogenation at higher temperatures. Nevertheless, in the beginning period of the reaction, one can still observe the formation of 3- β -D-glucopyranosyl-D-glucitol and glucose, and the latter became more dominant with increasing temperature, suggesting that the hydrolysis of cellobiose was more promoted at an increased temperature. It is also interesting to notice that GA appeared in the products of the cellobiose reaction at 453 and 473 K. In previous studies of cellulose conversion [24–31], GA was always rapidly hydrogenated to EG upon its formation. In contrast, GA was not instantly hydrogenated into EG in the present cellobiose reaction, which gave the decreased EG yield. The

Table 2

Reactivity of cellobiose and glucose catalyzed by H_2WO_4 and 1% Ru/C.

Reactant	Conversion (%)	Yield (%)				
		3- β -D-glucopyranosyl-D-glucitol	Sorbitol	Mannitol	EG	1,2-PG
Cellobiose	6.0	4.83	0.16	0	0	0
Glucose	11.1	0	9.74	0.08	0	0

Reaction conditions: 0.1 g H_2WO_4 , 0.3 g 1% Ru/C, 6 MPa H_2 , 1000 r/min, 393 K, 2 h.

Fig. 2. Product distribution versus time for cellobiose conversion at different temperatures. Reaction conditions: 0.10 g H_2WO_4 , 0.30 g Ru/AC, 6 MPa H_2 , 1000 r/min.

underlying reason may lie in that the retro-aldol condensation rate of cellobiose and its derived glucose is much higher than that of cellulose, which led to the production of excess GA. Since GA hydrogenation involves heterogeneous catalysis over Ru, the gas-liquid and liquid-solid mass transfer rate may lower the apparent hydrogenation rate although the activation energy of GA hydrogenation was only 42.6 kJ/mol. Increasing the Ru/C catalyst amount or by removing the possible mass transfer limitation is an effective way to accelerate GA hydrogenation and increasing the EG yield.

Fig. 3 presents the glucose conversion at different tempera-

tures. Similar to the cellobiose conversion, the direct hydrogenation of glucose also significantly prevailed over the C–C bond cleavage reaction at a relatively low temperature of 418 K, leading to the major production of sorbitol and minor production of EG. With the increase of the reaction temperature, the C–C bond cleavage reaction of glucose gradually dominated the hydrogenation leading to the major production of EG, similar to the case of cellobiose. However, on comparing the EG yields in the glucose and cellobiose reactions at the same conditions (Fig. 4.), we can find that the former is much faster than the latter in the initial periods of the reaction, suggesting that

Fig. 3. Product distribution versus time for glucose conversion at different temperatures. Reaction conditions: 0.10 g H_2WO_4 , 0.30 g Ru/AC, 6 MPa H_2 , 1000 r/min.

Fig. 4. Ethylene glycol yield as a function of reaction time for glucose and cellobiose conversion. Reaction conditions: 0.10 g H_2WO_4 , 0.30 g Ru/AC, 6 MPa H_2 , 1000 r/min.

Fig. 5. Ethylene glycol yields at 100% cellobiose or glucose conversion as a function of temperature. Reaction conditions: 0.10 g H_2WO_4 , 0.30 g Ru/AC, 6 MPa H_2 , stirring speed 1000 r/min.

the C–C bond cleavage reaction of glucose is much easier than that of cellobiose. Nevertheless, with the increasing of reaction time, the EG yield from cellobiose conversion surpassed that from glucose. Moreover, with an increase of the reaction temperature, the intersecting point of the EG yields of glucose and cellobiose shifted to a shorter reaction time (Fig. 4(b)–(f)), suggesting that a higher temperature is more favorable for the retro-aldol condensation of cellobiose in comparison with that of glucose. At each temperature, the final EG yield at 100% conversion of cellobiose was always higher than that of glucose, and the difference became larger at higher temperature (Fig. 5). This can be explained by the slow retro-aldol condensation of cellobiose as well as slow release of glucose from the hydrolysis of cellobiose, which is better matched with the subsequent hydrogenation of GA. On extrapolating this to cellulose conversion, this trend would hold if the hydrolysis of cellulose is much more difficult than cellobiose and the resulting glucose concentration in the solution is much lower, i.e., the EG yield would follow the order of cellulose > celloligosaccharides > glucose. However, this trend can be changed by tuning the ratio of H_2WO_4 to Ru/C as well as by optimizing the reaction conditions [34].

4. Conclusions

From an investigation of the hydrogenolysis of cellobiose to EG, we elucidated the reaction pathways in which hydrogenation, hydrolysis and retro-aldol condensation occurred simultaneously. DFT calculations suggested that the retro-aldol condensation of aldoses at the reducing end promoted the hydrolysis of the β -1,4-glycosidic bond. The comparison of the cellobiose and glucose reactions showed that the retro-aldol condensation of cellobiose is more difficult than that of glucose, which lowered the formation rate of glycolaldehyde and made it more matched with the subsequent hydrogenation rate, thus leading to increased yield of EG from cellobiose. This trend can be extrapolated to cellulose. This study provided useful information for the mechanistic understanding of cellulose conversion to EG and will guide the design of more efficient and selective catalyst formulations.

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Graphical Abstract

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Comparison of cellobiose and glucose transformation to ethylene glycol

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A new reaction pathway was proposed for cellobiose conversion. The retro-aldol condensation of cellobiose is more difficult than that of glucose, leading to increased yield of EG from cellobiose.

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纤维二糖与葡萄糖催化转化制备乙二醇

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摘要: 选用纤维二糖作为探针分子, 探索纤维素催化转化制备乙二醇过程的反应路径. 分别考察了纤维二糖和葡萄糖在双组分催化剂 H_2WO_4 和 Ru/C 下的催化反应活性. 结果表明, 乙二醇不仅来自于纤维二糖水解释产物葡萄糖的逆羟醛缩合作用, 同时也可以来自于纤维二糖的直接逆羟醛缩合过程. 而且, 纤维二糖的直接逆羟醛缩合作用对糖苷键的水解也有一定的促进作用. 比较发现, 钨基催化剂作用下纤维二糖的逆羟醛缩合反应活性比葡萄糖要低, 因此乙醇醛可以缓慢产生并在 Ru/C 催化剂上迅速加氢生成乙二醇. 使得以纤维二糖作为原料比以葡萄糖作为原料时获得更高的乙二醇收率.

关键词: 纤维二糖; 反应机理; 葡萄糖; 乙二醇

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