Catalytic Conversion of Concentrated Glucose to Ethylene Glycol with Semicontinuous Reaction System

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S *Supporting Information*

ABSTRACT: Catalytic conversion of biomass to bulk valuable chemicals is of great significance for humanity, alleviating the dependence on fossil energy resources. Herein, the catalytic conversion of concentrated glucose to ethylene glycol (EG) was studied with dual-functional catalysts in a semicontinuous reaction system. Among a variety of tungsten-based catalysts, AMT−Ru/AC gave the highest EG yield of 60.0% as the mole ratio of W to Ru active sites was in an optimal range of 5−8. Higher temperatures (over 200 °C) and lower concentration of reactant are beneficial to the EG production. The reaction kinetic study disclosed that the reaction selectivity dependent on temperature should be attributed to the big discrepancy in the activation energies between glycol aldehyde (GA, precursor of EG) and EG formation, while the selectivity sensitive to feedstock concentration should be primarily due to the GA side reactions which follow a higher order kinetics (pseudo second order) than the GA hydrogenation to EG (first order). The semicontinuous reaction system well controlled the reactants at low concentrations by a differential effect on the feedstock but realized the product concentration integral to the proceeding of the reaction. In this way, EG was effectively produced from concentrated glucose with high selectivity. Also, this reaction system was found to be suitable for the catalytic conversion of fructose to EG and propylene glycol. The present work provided a valuable strategy for the catalytic conversion of active biomass such as glucose and fructose to glycols, particularly for their practical applications on a large scale.

1. INTRODUCTION

With the depletion of fossil energy and the deterioration of the earth's environment, biomass, one of the major clean energy resources, has been considered to have great potential for use as an alternative feedstock to petroleum in the production of clean energy[1−4] and renewable chemicals.[5−9] Ethylene glycol (EG) is an important bulk industrial raw material, widely used in the synthesis of resins, automobile antifreeze, cosmetics, etc.[10] Its global consumption reached more than 21.0 million tons in 2011. Currently, EG is mainly produced from petroleum ethylene. It is highly important to realize EG industrial production in renewable ways.

Recently, a novel route for EG production from biomass was disclosed. Under hydrothermal conditions, cellulose was completely degraded with a high EG yield of 61% over tungsten carbide catalysts in the presence of 6 MPa H₂.[11,12] By using superior supports[13] or optimal catalyst preparation,[14] EG yields were promoted up to 75%. Furthermore, besides tungsten carbide catalysts, metallic tungsten and tungsten oxide based dual-functional catalysts are also found to be highly efficient for the cellulose conversion to EG.[15−17] More importantly, the tungsten oxide based catalysts have very good reusability and low cost of preparation.[17,18] All these works have paved a novel and solid road for the production of bulk valuable EG from biomass.

Glucose is the basic sugar unit composing biomass with content over 50%. It can be obtained from the hydrolysis of cellulose, starch of cassava or algae, cane sugar, etc. As a feedstock, it can be converted into energy chemicals such as ethanol,[19] sorbitol,[6,7] 1,2-propylene glycol,[20] and EG.[15] Compared to cellulose, glucose has many notable advantages in view of the chemical engineering process. First of all, glucose is highly water-soluble, which not only makes its transportation very convenient for chemical engineering operation, but also enables the products to be highly concentrated and consequently alleviate energy consumption in the following distillation for EG product separation. Second, glucose is more active than cellulose and does not need to undergo the rate-determining step of hydrolysis during catalytic conversion. This makes its conversion possibly take place at milder conditions and more efficiently than the cellulose conversion.

On the other hand, some notable problems accompany the advantages of glucose conversion. For instance, glucose has high chemical activity, which makes it readily undergo side reactions such as coking to form humins or tars under high reaction temperatures and high concentrations of reactant. As a result, the side reactions remarkably decrease the target EG production. Therefore, before this process really approaches commercialization, it is highly required to find right ways to settle such challenges.

In this work, we developed an efficient process to realize high-concentration glucose conversion to EG. In a semi-continuous reaction system and in the presence of optimal

Table 1. Cellulose, Glucose, and Fructose Conversions in Batch and Semicontinuous Reactors[a]

entry	reaction conditions	yield (mol % C)								
		EG	1,2-PG	Gly	1,2-But	Ery	Sor	Man	gas	total polyols
1	cellulose, batch	46.7	5.0	0	6.9	3.8	3.6	3.0	8.1	69.0
2	glucose, batch	7.0	4.9	2.4	2.8	0.8	32.5	7.0	8.1	57.4
3	glucose, semicont	50.2	9.4	2.1	6.3	3.3	1.1	2.9	3.8	75.3
4	fructose, batch	11.8	5.6	2.9	4.1	0	20.1	12.2	6.2	56.7
5	fructose, semicont	14.3	37.9	4.7	4.8	0	1.1	1.3	5.6	64.1

[a]Conditions: for entries 1−3, AMT (1000 ppm W), 4% Ru/AC (0.4 g), 240 °C, 5 MPa H_2, 40 min, 10% glucose solution, 2 mL/min; for entries 4 and 5, AMT (1000 ppm W), 4% Ru/AC (0.3 g), 240 °C, 5 MPa H_2, 40 min, 10% fructose solution, 0.667 mL/min.

tungsten-based dual-functional catalysts, concentrated glucose was successfully converted to EG with high yields. Some unique behavior of the reaction was observed under different reaction conditions and well interpreted based on reaction kinetics analysis. According to the strategy developed in the present work, a practical catalytic process for catalytic conversion of sugars including glucose and fructose to EG could be developed for large scale industrial applications.

2. EXPERIMENTAL SECTION

2.1. Catalyst Preparation. Catalysts Ru/activated carbon (AC), Pt/AC, Pd/AC, and Ir/AC were prepared by the incipient wetness impregnation method. Before impregnation, the activated carbon support (NORIT, surface area 709 m^2/g) was treated in nitric acid solution (33 wt %) at 80 °C for 24 h and then dried at 120 °C. Ruthenium chloride, chloroplatinic acid, palladium chloride, and chloroiridic acid were used as metal precursors, respectively. The impregnated samples were dried at room temperature overnight and at 120 °C for 12 h. The as-prepared catalysts were reduced in a H_2 gas flow at 350 °C for 1 h, and passivated in a 1% O_2/N_2 gas flow for 4 h at room temperature before exposure to air. Raney Ni (Raney 3111) was provided by Grace Davison.

Ammonium metatungstate (AMT) was provided by Chenzhou Diamond Tungsten Products Co. Ltd. Tungsten acid, phosphotungstic acid, and silicotungstic acid were provided by Sinopharm Chemical Reagent Co. Ltd.

2.2. Catalyst Characterization. The active sites of metal catalysts were determined by CO chemisorptions on a Micromeritics Autochem 2920 apparatus.

2.3. Catalytic Reaction. Catalytic conversion of glucose was typically carried out in a semicontinuous reaction system. Catalysts and 20 mL of water were preloaded in a stainless-steel autoclave (Parr Instrument Co., 100 mL). Then, the reactor was filled with 5 MPa H_2 after expelling air with H_2 five times. When the reactor was heated to the reaction temperature, 20 mL of glucose (Sinopharm Chemical Reagent Co. Ltd.) aqueous solution (10 wt %) feedstock was injected into the reactor with a high pressure pump (Shimadzu LC-20AT). The reactant solution was stirred at rate of 1000 rpm. The overall time of injection and reaction was 40 min.

For comparison, a batch reactor was also employed to conduct the reaction. The reaction procedure has been described elsewhere.[11,12] Catalysts, water, and glucose were added to the reactor with 5 MPa H_2 and stirred at rate of 1000 rpm. Then, the reactor was heated to the reaction temperature and maintained for 40 min.

2.4. Kinetic Studies. Kinetic studies were carried out in the semicontinuous reaction system. Catalysts (AMT (1000 ppm W) for retro-aldol condensation and side reactions, 0.4 g of 4% Ru/AC for hydrogenation) and 20 mL of water were preloaded

in a stainless-steel autoclave (Parr Instrument Co., 100 mL). Then, the reactor was filled with 4 MPa H_2 after expelling air. Feedstock of 20 mL of glucose (Sinopharm Chemical Reagent Co. Ltd.) aqueous solution (10 wt %) or glycolaldehyde aqueous solution (4 wt %) was injected into the reactor at a speed of 10 mL/min at the reaction temperatures. Then, real-time sampling was conducted (1 mL per time) during the reaction with an interval of 1−5 min.

2.5. Product Analysis. After the reaction, the liquid products were analyzed with liquid chromatography (Agilent 1200 HPLC equipped with Shodex Sugar SC1011 column and refractive index detector). The gas products were analyzed with gas chromatography (Agilent 6890N, TDX-1 column, thermal conductivity detector). The yield of products was calculated based on the carbon weight mole ratio.

3. RESULTS AND DISCUSSION

3.1. Influence of Reactor. The catalytic conversion of glucose to EG was first evaluated with a batch reactor. As shown in Table 1, in the presence of a composite catalyst of AMT−4% Ru/AC, glucose was mainly converted into hexitols (sorbitol and mannitol) with an overall yield of 39.5% (more detailed data are listed in the Supporting Information, Table S1), in contrast to an EG yield as low as 7.0%. This is quite different from the case of cellulose conversion which predominantly produced EG at a yield of 46.7%. The reason for the difference should be attributed to the active property of glucose, which readily undergoes hydrogenation to form stable sorbitol at temperatures as low as 80 °C in the presence of a Ru/AC catalyst.[21]

In fact, the catalytic conversion of glucose to produce EG needs to undergo a critical step (Scheme 1, R1), i.e., retro-aldol condensation (RAC) to form glycolaldehyde (GA), which mainly happens at temperatures higher than 160 °C.[15,17,22]

Scheme 1. Reaction Mechanism of Glucose Catalytic Conversion to EG
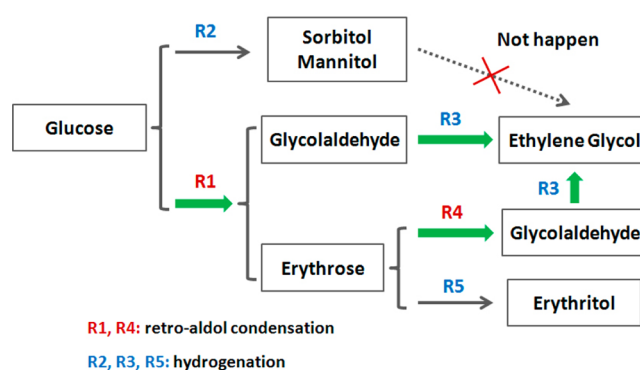
However, during heating of the batch reactor from room temperature to the target 240 °C, a large portion of glucose has been first hydrogenated into sorbitol, which is quite stable and cannot be further converted into EG under the present reaction conditions.[15] For cellulose conversion, it is relatively stable until the hydrolysis reaction takes place at temperatures higher than 150 °C,[6,7,23] at which the RAC reaction can also take place. Thus, the balance between the RAC reaction and hydrogenation of glucose has a great impact on the polyol yield distribution in the final products.

On the basis of the above analysis of glucose conversion in a batch reactor, we optimized the reaction system by employing a semicontinuous reactor to effectively control the reaction temperatures, meanwhile conveniently controlling the reactant concentration during the reaction. As compared in Table 1, EG was the major product with 50.2% yield in the semicontinuous reaction system. Furthermore, the overall polyol yields were also notably promoted compared to that in the batch reactor, indicating that the side reactions such as humin formation were depressed effectively. The underlying essential reasons for such good performance of the semicontinuous reactor for glucose conversion to EG were further studied and are discussed in sections 3.4.1 and 3.4.3.

3.2. Evaluation of Various Catalysts. It has been disclosed that dual-functional catalysts of W−M(8,9,10) are effective for the biomass conversion to EG,[15−18] where the tungsten species play a critical role in sugar degradation, i.e., RAC, to selectively form glycolaldehyde (GA), while the hydrogenation catalysts convert GA to EG. Herein, the effect of different hydrogenation catalysts, tungsten species, and their mole ratios on the EG yield were investigated.

3.2.1. Hydrogenation Catalyst Screening. As shown in Figure 1, the noble metal catalysts of 4% Ru/AC, 4% Pt/AC,
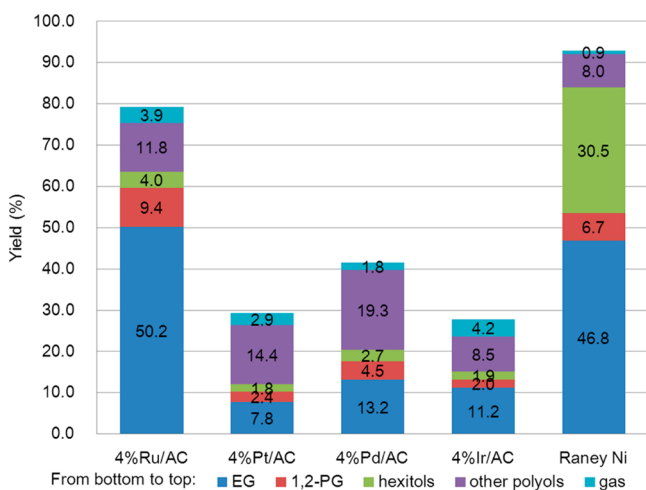

Figure 1. Glucose conversion over AMT−M(8,9,10) catalysts. Conditions: AMT (1000 ppm W), 240 °C, 5 MPa H$_2$, 40 min, 10% glucose solution, 2 mL/min.

4% Pd/AC, and 4% Ir/AC gave different catalytic performances when combined with ammonia metatungstate (AMT). AMT− 4% Ru/AC showed the highest polyol yield and EG selectivity in contrast to the much lower EG and polyol yields of the other three composite catalysts. The CO chemisorption measurements shows that the metal dispersions were quite different, i.e., 30.3, 4.5, 11.0, and 30.5% for the Ru, Pt, Pd, and Ir catalysts, respectively, even though they had the same metal loading.

Evidently, the difference in EG yields is related to not only the metal dispersion, but also the essential activity for the catalytic hydrogenation under hydrothermal conditions. The good performance of Ru/C in glucose conversion to EG is well consistent with the fact that ruthenium catalysts have been widely used in glucose hydrogenation for sorbitol industrial production.[24]

In addition, the less expensive catalyst AMT−Raney Ni also showed a very high polyol yield. However, a much greater amount of hexitols was formed compared to that formed with AMT−4% Ru/AC. Since the polyol product distribution can be tuned by changing the ratio of W to M(8,9,10),[15] the AMT− Raney Ni catalyst might also be suitable for glucose conversion to EG upon optimizing the Ni−W ratios.

3.2.2. W-Based Catalyst Screening. As shown in Figure 2, four tungsten compounds were evaluated in the glucose
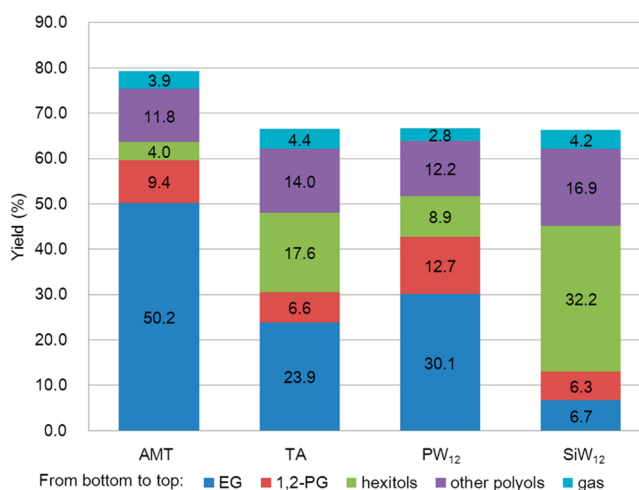

Figure 2. Glucose conversion over 4% Ru/AC in combination with different W-based catalysts. Conditions: 4% Ru/AC (0.4 g), W compounds (corresponding to 1000 ppm W), 240 °C, 5 MPa H$_2$, 40 min, 10% glucose solution, 2 mL/min.

conversion in combination with 4% Ru/AC as the hydrogenation catalyst. Among the compounds of AMT, tungstophosphoric acid (PW$_{12}$), tungsten acid (TA), and tungstosilicic acid (SiW$_{12}$), AMT showed the best performance. Very intriguingly, the SiW$_{12}$−Ru/AC catalysts seemed to fail in selectively producing EG but formed a large amount of hexitols in the reaction. It has been found that the RAC reaction takes place in the presence of tungsten species via homogeneous catalysis;[17,25] the performance of tungstosilicic acid indicates that the catalytic function of tungsten can be remarkably depressed by some ions in the solution.

Regarding the TA−Ru/AC catalyst, although it gave high EG yields in cellulose conversion,[17] its performance in the glucose conversion to EG was not excellent. This might be related to the low solubility of TA,[17] which could not provide sufficient tungsten species in the solution for the catalysis of highly concentrated glucose feedstock.

Thus, on the basis of the results of catalyst screening, the dual-functional catalyst of AMT−Ru/AC was selected as the superior one for further study in glucose conversion.

3.3. Effects of W−Ru Active Site Ratio. The influence of the W−Ru ratio on the EG yield was studied by separately changing the amount of each active component in the composite catalyst of AMT−Ru/AC. The W−Ru ratio was
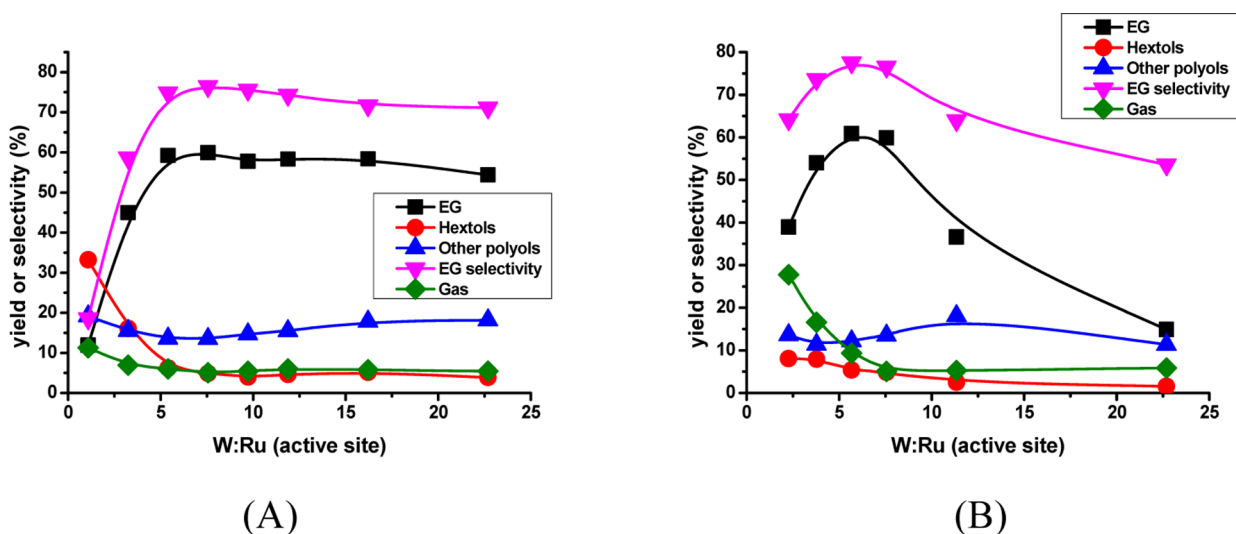
(A)　　　　　　　　　　　　　　　　　　(B)

Figure 3. Effects of W−Ru active sites ratio on glucose conversion. (A) Varying W/Ru ratio with Ru/AC amount fixed at 0.3 g. (B) Varying W/Ru ratio with AMT amount fixed at 1167 ppm W. Conditions: 240 °C, 5 MPa H₂, 40 min, 10% glucose solution, 0.667 mL/min. Selectivity of EG = yield of EG/overall yield of polyols.

calculated based on the numbers of tungsten atoms and Ru active sites (determined by CO chemisorptions) put into the reactor. As shown in Figure 3A, with the increase of AMT amount used, the EG yield increased significantly and leveled off around 60% at the expense of the sorbitol yield, which decreased from 35% to less than 5%. High EG yields were obtained with the W−Ru ratio in the range 5−8. Further increasing the AMT amount led to a slight decrease in the overall yield of polyols and the EG selectivity.

Figure 3B shows the results of experiments varying the W/Ru ratio with the AMT amount fixed. The EG yield showed a volcano-shaped curve with the amount of Ru/AC increase. When the amount of Ru/AC was too low, it was insufficient for the catalytic hydrogenation, leading to merely a small portion of reactive intermediates hydrogenated into EG. When the Ru/AC amount increased, the EG yield was improved and reached high values as the W−Ru ratios were in the range 5−8. A greater amount of Ru/AC reduced the EG yield because of much gas formation by catalytic methanation over the Ru/AC catalyst.

Therefore, the W−Ru ratios in the range 5−8 were suitable for the catalytic conversion of glucose to EG over the AMT−Ru/AC catalyst.

3.4. Effects of Reaction Conditions. *3.4.1. Effects of Reaction Temperature.* The influence of reaction temperature is shown in Figure 4. When reactions were conducted at 180−240 °C, the overall polyol yields leveled off at ca. 87%. However, the EG selectivity underwent dramatic changes with temperature increase. At 180 °C, hexitols were the main products in contrast to a minor EG yield. Once the reaction temperature rose to higher than 200 °C, EG product overwhelmed hexitols with high yields up to 60.0%.

As shown in Scheme 1, the hydrogenation of glucose to form hexitols (R2) is competing with the glucose degradation (R1) to form GA, which further forms EG via catalytic hydrogenation.[15,17] The reaction selectivity significantly depending on temperatures indicates that there is a big discrepancy in the activation energies (Ea) between the reaction paths of R1 and R2, which leads to different responses in the reaction rate to changes in the reaction temperature.
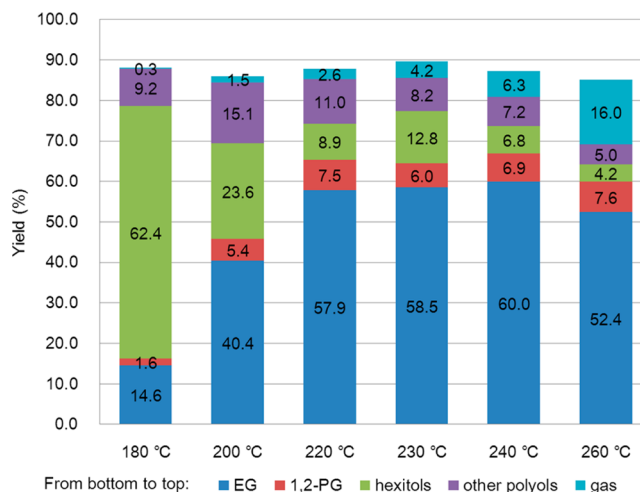

Figure 4. Glucose conversion at different temperatures. Conditions: AMT (1000 ppm W), 4% Ru/AC (0.3 g), 240 °C, 5 MPa H₂, 40 min, 10% glucose solution, 0.667 mL/min.

Actually, our kinetics study (Figure 5) disclosed that the apparent activation energy of R1 was 148.0 kJ/mol, nearly 4-fold that of R2. This well interprets the phenomenon that the reaction selectivities to sorbitol and to EG change reversely with temperature increase. A more detailed kinetics study is under way.

In addition, further increasing the temperature to 260 °C decreased the overall yield of polyols and EG yield but notably increased the gas production. This should be related to the enhancement of polyol hydrogenolysis over Ru catalyst and glucose coking at overly high temperatures.

3.4.2. Effects of H₂ Pressure. As shown in Figure 6, the H₂ pressure had a significant influence on the glucose conversion results. Particularly when the pressure was lower than 1 MPa, the total polyol yield was merely ca. 25%. Furthermore, more than 55% carbon in the products could not be quantified with HPLC or GC analysis, which should be mainly attributed to the humin or polymer formation.
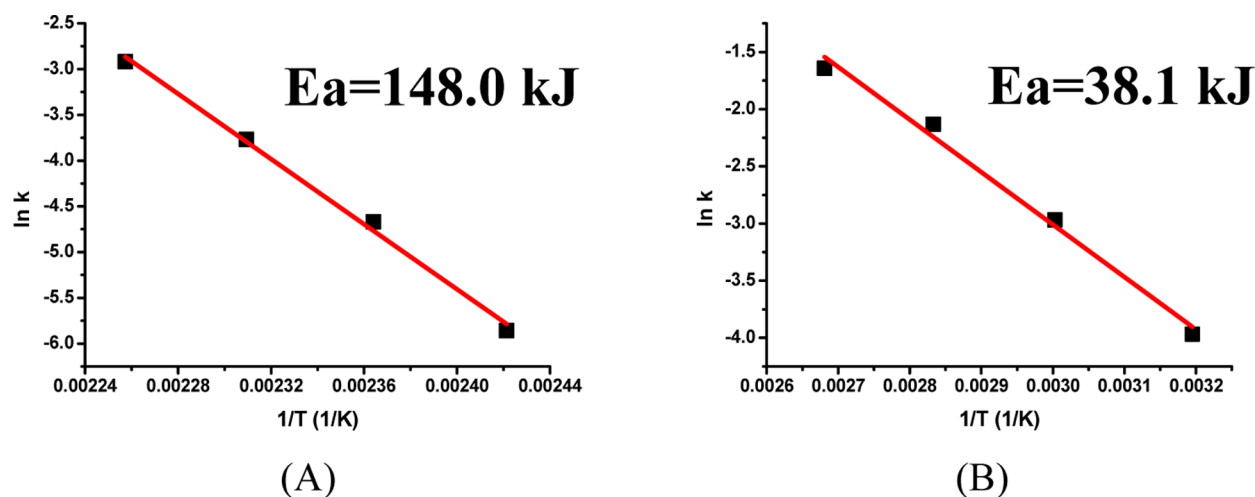
Figure 5. Arrhenius curves and apparent activation energies of (A) glucose retro-aldol condensation and (B) glucose hydrogenation. Conditions: (A) 140−170 °C, 4 MPa H_2, initial glucose concentration 5 g/L, AMT (1000 ppm W), sample interval 3 min; (B) 40−100 °C, 4 MPa H_2, initial glucose concentration 5 g/L, AMT (1000 ppm W), 4% Ru/AC (0.4 g), sample interval 3 min.
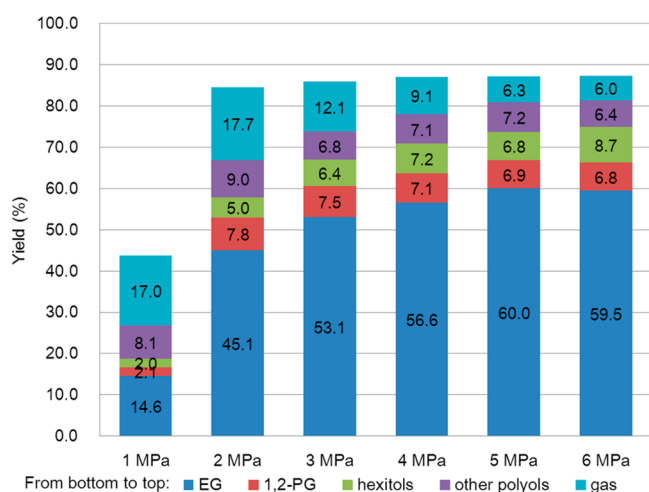

Figure 6. Glucose conversion under different H_2 pressures. Conditions: AMT (1000 ppm W), 4% Ru/AC (0.3 g), 240 °C, 5 MPa H_2, 40 min, 5% glucose solution, 0.667 mL/min.
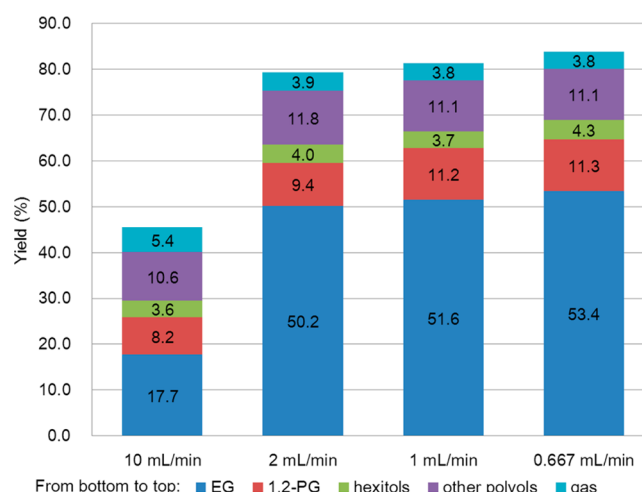

Figure 7. Glucose conversion with different feeding speeds. Conditions: AMT (1000 ppm W), 4% Ru/AC (0.4 g), 240 °C, 5 MPa H_2, 40 min, 10% glucose solution.

Increasing the H_2 pressure to 2 MPa or higher remarkably improved the overall yields of polyols and EG. Under 5−6 MPa H_2 pressure, the EG yields reached a high value of 60.0%. In addition, with the H_2 pressure increase, gas product, especially CO_2, yields were reduced (see the Supporting Information, Table S1).

3.4.3. Effects of Glucose Feeding Speed. For the semi-continuous reaction system, the feeding speed of feedstock will largely determine the process efficiency; meanwhile, it will change the reactant concentration and might influence the reaction selectivity. Figure 7 shows the results of glucose conversion under different feeding speeds. When the glucose solution was fed into the reactor at a rate of 10 mL/min, the EG yield was merely 17.7%. Slowing the feeding speed to 2 mL/min remarkably improved the EG yield to higher than 50%. However, comparing the results between low and high feeding speeds, one may notice that the yields of other poylols did not change as significantly as the EG yield did. This suggests that more side reactions take place in the course of the cascade reactions for EG formation.

As shown in Scheme 1, under tungsten catalysis, glucose is degraded to GA via the RAC reaction. GA is an unstable chemical under high temperature conditions, readily undergoing polymerization or degradation provided it is not being timely hydrogenated into the relatively stable EG product. At a high feeding speed of glucose, the concentrations of glucose and the derived GA are simultaneously improved in the reactor, leading to the the increase in the rates of both the GA hydrogenation and the side reactions of GA. However, we disclosed that the hydrogenation of GA to form EG followed a reaction order different from that of the global side reactions of GA (Figure 8). The hydrogenation of GA to EG is a pseudo-first-order reaction, whereas the global side reactions of GA follow pseudo-second-order kinetics. This means that the rate of global side reactions of GA is more sensitive to reactant concentrations and will be improved more significantly than the GA hydrogenation does with GA concentration increase. Therefore, a low feeding speed of glucose keeps the GA concentration at a low level, effectively depresses side reactions of GA, and consequently produces EG with a high yield.
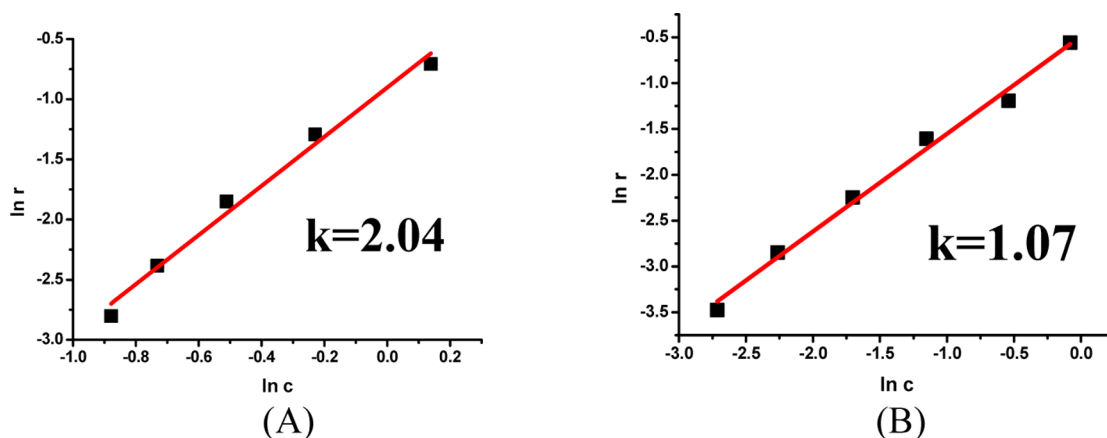
Figure 8. Reaction orders determined by differential method for (A) GA side reactions (second order) and (B) GA hydrogenation (first order). Conditions: (A) 220 °C, 4 MPa H_2, initial GA concentration 5 g/L, AMT (1000 ppm W), sample interval 1 min; (B) 60 °C, 4 MPa H_2, initial GA concentration 5 g/L, AMT (1000 ppm W), sample interval 1 min.

The semicontinuous reaction system can effectively control the concentration of active intermediate by a differential of the feedstock concentration during the reaction. On the other hand, this reaction system can realize integration of the EG concentration. In this way, glucose can be effectively converted into EG with a high yield and high concentration. Although the glucose concentration in this study was typically 10%, we promoted it to a much higher concentration (50%) and found that no loss in EG yield was caused if only the real-time concentration of glucose in the reaction system was kept at a low level.

3.5. Different Sugar Feedstock Conversions. Similar to glucose, fructose is also an important basic unit of biomass, such as in Jerusalem artichoke tubers, and could be used for polyol production. Now that the semicontinuous reaction system can effectively realize the unstable reactant of glucose conversion to EG with high yields under a high concentration, we further employed it for the fructose conversion, which is even more active than glucose.

As compared in Table 1 (entries 4 and 5), in the batch reactor, fructose was mainly converted into hexitols in the presence of AMT−Ru/AC. In contrast, it was mainly converted into 1,2-propylene glycol (1,2-PG) in the semicontinuous reactor. This is consistent with the results of Jerusalem artichoke tuber conversion.[26] On the other hand, the total polyol yield was higher than that obtained in the batch reactor. Evidently, the semicontinuous reactor system has a universal validity in the catalytic conversion of biomass, particularly for active and unstable feedstock such as glucose and fructose conversion to glycols.

4. CONCLUSIONS

We have disclosed an effective semicontinuous reaction system for the catalytic conversion of highly concentrated glucose feedstock into EG. Compared with the batch reactor previously widely employed in biomass conversion to EG, the semicontinuous reaction system significantly improves the yield of EG through suppressing side reactions of sorbitol and coke formation. In the presence of the dual-functional catalyst AMT−Ru/AC, EG can be obtained at yield of 60.0% with an overall polyol yield of 80.8%.

The reaction temperature and feeding speed of glucose have significant impacts on the EG production. There is a critical temperature point for the glucose conversion to EG, above which EG is predominantly formed over hexitol production. The big discrepancy in activation energies for EG formation and sorbitol formation accounts for such dramatic changes in selectivity versus reaction temperatures. Keeping the concentration of glucose at low levels during reaction is critical for obtaining EG production with high yields, which can be attributed to the reaction intermediates undergoing EG formation reaction and side reactions with different reaction orders. The semicontinuous reaction system is competent for the catalytic conversion of glucose and fructose to EG and 1,2-PG with high concentrations. The present work gives very valuable guidance for designing a catalytic process for the conversion of chemically active biomass, particularly for applications at industrial scales.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed data of sugar catalytic conversion to EG and 1,2-PG under different conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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