Reaction Route Selection for Cellulose Hydrogenolysis into C₂/C₃ Glycols by ZnO-Modified Ni-W/β-Zeolite Catalysts

Minyan Gu¹, Zheng Shen¹, Long Yang¹, Wenjie Dong², Ling Kong¹, Wei Zhang¹, Bo-Yu Peng¹ & Yalei Zhang¹,³

A β-zeolite-supported nickel and tungsten catalyst (Ni-W/β) was employed to generate C₂/C₃ glycols (ethylene and propylene glycols) in a satisfactory yield from cellulose. After optimizing the acidity of the support, the Ni-W synergy and the co-catalyst, the yield of C₂/C₃ glycols reached 70.1% (C %), with propylene glycol accounting for 51.1% of the product. This performance was attributed to the effective control of the major reaction steps, namely, hydrolysis, isomerization, retro-aldol condensation and hydrogenation, by the tailored Ni-W-ZnO/β catalyst. The characterization and reaction results indicated that the cellulose hydrolysis step was promoted by the appropriate acidic sites of the β-zeolite, and the reaction routes to C₂/C₃ glycols were influenced by the mass loading of Ni-W through the synergy of nickel and tungsten oxide, in which Ni is effective in the hydrogenation while W facilitates bond cleavage via a retro-aldol condensation (C₆ to C₂/C₃). Moreover, with the leaching of metal during four cycles of reuse, the catalytic performance was also influenced by the synergy of Ni and W. In addition, the isomerization of glucose to fructose was promoted by ZnO and afforded a high yield of propylene glycol.

With diminishing fossil resources and increasing environmental concerns worldwide, searching for alternative fuels has attracted great interest in recent years. As a vital renewable alternative to fossil fuels, cellulose is the most abundant source of biomass and has received considerable attention. Consequently, different conversion routes for cellulose have been explored to achieve high energy efficiency and atom economy. Cellulose has been selectively converted into different chemicals, such as oligomers, glucose, HMF, sorbitol, hexitols and C₂/C₃ glycols (ethylene glycol and propylene glycol, EG/PG) through a series of chemical reactions, including hydrolysis, dehydration and hydrogenolysis. Among them, the hydrogenolysis of cellulose to C₂/C₃ glycols is particularly noteworthy because of the versatile applications of glycols directly and as platform molecules in the synthesis of fuels and value-added products, including polyesters and antifreeze.

The catalytic conversion of cellulose is a complex reaction network comprising hydrolysis, retro-aldol condensation, hydrogenation, isomerization, dehydrogenation, thermal side reactions, etc. In addition to C₂/C₃ glycols, a variety of by-products, such as sorbitol, mannitol, xylitol, 1,2-butanediol, and glycerol, can be coproduced. Based on previous studies, three reaction steps are critical for cellulose conversion to EG: hydrolysis, retro-aldol condensation, and hydrogenation. For PG, the isomerization of glucose is also involved. To enhance the above reaction steps and increase the yield of C₂/C₃ glycols, a series of effective metals or metallic oxides, such as tungsten derivatives, tin derivatives, lanthanides, niobium and zinc, were employed in the catalytic system. Deng et al. modified Pt/Al₂O₃ and Ni/Al₂O₃ catalysts by SnO₂ to enhance the conversion of cellulose to C₂/C₃ glycols. Using these two catalysts, carbon selectivity of C₆ products decreased from 43.3 to 0.8% and 63.3 to 0.2%, respectively, which indicated that SnO₂ played a significant role in C-C bond cleavage via retro-aldol...
glycol carbon yields of 32.8%, 52.4%, 12.8%, 62.0% and 43.9%, respectively. WOx was introduced onto a Pd/Al2O3 catalyst by Liu et al. to obtain in the Sn-enhanced retro-aldol condensation step. In addition to Sn species, W species also facilitated cleavage of the C3-C3 bond in C6 sugars should occur, not C2–C4. Then, after the C-C bond cleavage in the sugars via a retro-aldol condensation (C6 to C2/C3), hydrogenation occurs immediately to generate C2/C3 glycols, avoiding the occurrence of other side reactions. When the reaction reached this point, further C-C bond cleavage should not occur. Otherwise, smaller molecules could be generated from the C2/C3 glycols. Furthermore, as a more valuable product, PG is more difficult to produce because the cleavage of the C2–C3 bond in C6 sugars should occur, not C2–C4.

Herein, to balance the hydrolysis, retro-aldol condensation and hydrogenation and to realize the selective conversion of cellulose into C2/C3 glycols, three aspects will be investigated and discussed: 1) a tailored catalyst will be designed and synthesized, including support selection, support structure modification, control of the Ni-W synergy and co-catalyst screening; 2) the effect of the above factors on the reaction route and the overall mechanism will be studied via a series of catalytic reactions and analyses; 3) the reuse performance and the relationship between Ni-W leaching and product distribution during reuse will be utilized to verify the effect of Ni-W on reaction route selection.

Results and Discussion

The effect of the acidity of the β-zeolite. Because of the obvious importance of the catalytic support, which not only physically supports and improves the dispersion of the metal but also provides acid sites, different supports (Al2O3, TiO2, SiC, ZSM-5, and raw β-zeolite) were screened to determine the optimum combination for cellulose and glycols based on Ni-W bimetallic synergy. As displayed in Fig. 1, mannitol (M), sorbitol (S), EG and PG (C2/C3 glycols) as the major alcohol products were exhibited. There was a significant difference between the total yield of M, S, PG and EG, the yields of C2/C3 glycols, and the conversions obtained with Ni-W/SiC, Ni-W/TiO2, Ni-W/ZSM-5, Ni-W/Al2O3 and Ni-W/raw-β catalysts. Ni-W/raw-β exhibited the highest reactivity. To understand the reason for the superiority of Ni-W/raw-β, the physicochemical properties of the catalysts were investigated, as displayed in Table S1 (entries 1 to 6). The total loading of Ni and W remained the same for each case, whereas BET surface area and acidity varied considerably between catalysts. The BET surface areas of Ni-W/SiC,

![Figure 1. Catalytic reactions on different supports. Reaction conditions: 30 min, 6 MPa H2, 245 °C, 50 mL of H2O, 0.5 g of cellulose, 0.15 g of catalyst. EG: ethylene glycol; PG: 1,2-propylene glycol; S: sorbitol; and M: mannitol. Other products not listed include methane, methanol, ethanol, 1-propanol, glycerol, 1,2-butanediol, erythritol, 1,2-pentanediol, 1,2-hexanediol, furfural, furen and other unknown products.](https://doi.org/10.1038/s41598-019-48103-6)
the performance of Ni-W/
This result suggested that not only the quantity of acid sites but also the strength of the acid sites would influence
that the strength of the acid sites was enhanced by dealumination, although the quantity of sites did not increase.
β
Figure S1(a) shows the ammonia desorption peaks of Ni-W/
empty sites for the loading of other metals (e.g., Ni and W) and redistribution of the acid sites in the catalysts. As
β
Figure 2, although both the Brønsted acidity (1540 cm
-1) of Ni-W/TiO2, Ni-W/ZSM-5, Ni-W/Al2O3 and Ni-W/raw-β were 0.15, 0.17, 0.62 and 1.71 mmol/g, respectively, and the total yields of C2/C3 glycols, manniitol and sorbitol were 37.9%, 40.5%, 45.6%, 50.1% and 61.2%, respectively. The results suggested that there was no obvious correlation between the BET surface area and the reactivities on different supports, indicating that the surface area was not the primary cause of the superiority of Ni-W/raw-β.

The synergistic effect of Ni and W. As mentioned above, the acid sites played an important role in the production of glycols, especially in the acidic hydrolysis of cellulose. Therefore, we firstly investigated the synergistic effects of Ni and W on the acid sites. As shown in Fig. 2, although both the Brønsted acidity (1540 cm
-1) and Lewis acidity (1492 cm
-1) of raw β-zeolite were removed during the dealumination by HNO3 solution, Ni-W/β still showed higher glycol yields than the other catalysts (Fig. 1), which may be attributed to the function of the Ni and W species in the acid sites. The assumption is confirmed by the data in Fig. 2; after the loading of Ni or W, great changes occurred in the acidity of the catalyst, suggesting that Ni provided abundant Lewis acid sites in the β-zeolite and that W provided both Brønsted and Lewis acid sites, which could ensure the success of cellulose hydrolysis and hydrogenolysis. Moreover, Fig. 1 shows that Ni-W/β exhibited high catalytic activity, but Ni/β and W/β both exhibited low activity, which indicated that Ni-W bimetallic synergy, and not the individual effects of Ni or W, facilitated the C2/C3 glycols production. In order to more clearly explain the synergy of Ni and W on acidity, the NH3-TPD experiment was showed in Figure S1(b). Similar to Py-IR result, after dealumination, β lost almost all of its acidity. The only small peaks near 150 °C might attributed to the OH groups formed by aluminia vacancy, which was similar to the H peaks in Py-IR. After the loading of Ni or W on β (deAl), the catalytic

![Figure 2.](image-url)
The effect of co-catalysts on product distribution. Although the conversion of cellulose into glycols has been widely studied, controlling the $C_3/C_2$ distribution has received less attention, and the increase of PG yield is hard because rigorously controlling the C-C bond cleavage position is important. Hence, to control the position of C-C bond cleavage to increase the selectivity of PG and investigate the influence of these co-catalysts on the $C_2/C_3$ glycols distribution, a series of metal oxides and alkalis were added into the Ni-W/β system, as displayed in Table 1. ZnO, Fe$_3$O$_4$, MgO and alkalis gave rise to improved yields of C3 glycols from 19.3 to 35.8, 24.1, 23.2, 26.8, 29.3 and 32.1%, and the yields of C2/C3 glycols improved from 64.6 to 70.1 and 65.3%.

Figure 3. Catalytic reaction performance over the Ni-W/β catalysts with various Ni-W loading. Reaction conditions: 30 min, 6 MPa H$_2$, 245 °C, 50 mL of H$_2$O, 0.5 g of cellulose, 0.15 g of catalyst. EG: ethylene glycol; PG: 1,2-propylene glycol; S: sorbitol; M: and mannitol.
with ZnO and Fe₃O₄, respectively. Among these co-catalysts, ZnO significantly influenced the C₂/C₃ glycols distribution and PG yield, which was further investigated. First, the effect of the ZnO dosage was tested, as shown in Figure S4. Opposite trends in the PG and EG distribution were observed because the PG yield (C₃) increased significantly with the addition of ZnO, while the EG (C₂) yield obviously decreased. The balance between the yields of PG and EG indicated that PG was preferentially obtained in the presence of ZnO, i.e., the selective generation of PG and EG was influenced by ZnO²⁷. Furthermore, LA, another C₃ product, could not be generated when there was no ZnO in the system. In addition, its yield increased with increasing ZnO dosage (less than 200 mg). Therefore, from the increasing trends in the yields of PG (C₃) and LA (C₃) and the decreasing trends in the yields of EG (C₂) and S (C₆), we can infer that ZnO selectively promoted the formation of C₃ products via C₃-C₃ bond cleavage from C₆. Since there are few reports about the specific role of ZnO²⁸,²⁹, we further investigated the mechanism of the effect of ZnO in the mechanism section.

**Reaction mechanism.** The proposed reaction route for the formation of C₂/C₃ glycols from cellulose using Ni-W/β in the presence of ZnO is shown in Fig. 4. Based on this reaction route, the final products, EG, PG, sorbitol and mannitol, were produced by route 1 (R1: hydrolysis, R2: retro-aldol condensation and R3: hydrogenation), route 2 (R1: hydrolysis, R4: isomerization, R2, R4/R3 and R3) and route 3 (R1 and R3), respectively. Figure 1 shows that when β-zeolite served as the support, the maximum total yield of the four final products was obtained. We conjectured in support section above that the excellent performance of β-zeolite might be attributed to the enhancement of

| Entry | Catalyst | Conversion (%) | Yield (%) | EG | PG | S | M | Glycols | PG/Glycols (%) |
|-------|----------|---------------|-----------|----|----|---|---|---------|----------------|
| 1     | None     | 74.0          | 0.0       | 0.0 | 0.0 | 0.0 | 0.0 | 0.0     | 0.0            |
| 2     | Ni-W/β   | 100.0         | 45.3      | 19.3| 11.7| 3.4 | 64.6| 29.9    |                |
| 3     | Ni-W/β + ZnO | 100.0         | 34.3      | 35.8| 6.6 | 7.3 | 70.1| 51.1    |                |
| 4     | Ni-W/β + Fe₃O₄ | 100.0         | 41.2      | 24.1| 17.0| 10.1| 65.3| 36.9    |                |
| 5     | Ni-W/β + MgO | 100.0         | 39.8      | 23.2| 10.5| 5.6 | 63.0| 36.8    |                |
| 6     | Ni-W/β + Al₂O₃ | 100.0         | 43.3      | 10.7| 14.7| 3.5 | 54.0| 19.8    |                |
| 7     | Ni-W/β + TiO₂ | 100.0         | 41.7      | 12.6| 10.8| 7.8 | 54.3| 23.2    |                |
| 8     | Ni-W/β + NaOH | 100.0         | 23.3      | 26.8| 4.9 | 4.8 | 50.1| 50.1    |                |
| 9     | Ni-W/β + Ca(OH)₂ | 100.0         | 27.8      | 29.3| 6.2 | 9.8 | 57.1| 51.3    |                |
| 10    | Ni-W/β + Ba(OH)₂ | 100.0         | 25.7      | 32.1| 4.1 | 6.2 | 57.8| 55.5    |                |

Table 1. The catalytic performance of co-catalysts based on Ni-W/β. Reaction conditions: 30 min, 6 MPa H₂, 245 °C, 50 mL of H₂O, 0.5 g of cellulose, 0.15 g of catalyst, 100 mg of co-catalysts. EG: ethylene glycol; PG: 1,2-propylene glycol; S: sorbitol; and M: mannitol.
which is attributed to the H metal-catalysed liquid-phase reactions for the following two major reasons: 1) the catalyst can readily leach metal, 2) the complex intermediate compounds produced by the side reactions can block the pores and poison the catalyst. Therefore, it could be concluded that the acidity of Ni-W/raw-β enhanced cellulose hydrolysis. Furthermore, as the strength of the acidity was enhanced by dealumination, Ni-W/β provided a higher pseudo yield of the hydrolysis than that obtained with Ni-W/raw-β.

| Entry | Catalyst       | Reactant  | Yield (%) | EG | PG | S  | M  |
|-------|----------------|-----------|-----------|----|----|----|----|
| 1     | Ni-W/β         | Sorbitol  | 0.0       | 6.0| 95.0| 0.0| 0.0|
| 2     | Ni-W/β         | Mannose   | 12.3      | 8.9| 1.3| 51.5|
| 3     | Ni-W/β         | Glucose   | 51.0      | 14.5| 8.8| 1.7|
| 4     | Ni-W/β+ZnO     | Glucose   | 28.9      | 35.7| 7.2| 2.3|
| 5     | Ni-W/β         | Fructose  | 13.2      | 48.7| 10.2| 8.9|
| 6     | Ni-W/β+ZnO     | Fructose  | 12.9      | 49.2| 9.9| 9.5|
| 7     | Ni-W/β         | Dihydroxyacetone | 0.0 | 69.8| —| —|
| 8     | Ni-W/β+ZnO     | Dihydroxyacetone | 0.0 | 71.2| —| —|
| 9     | Ni-W/β         | Acetol    | 0.0       | 88.7| —| —|
| 10    | Ni-W/β+ZnO     | Acetol    | 0.0       | 87.4| —| —|

Table 2. Conversion of different carbohydrates as probe reactants over Ni-W/β. Reaction conditions: 30 min, 6 MPa H$_2$, 245 °C, 50 mL of H$_2$O, 0.5 g of reactant, 0.15 g of catalyst, and 100 mg of ZnO. EG: ethylene glycol; PG: 1,2-propylene glycol; S: sorbitol; and M: mannitol.

To further understand the mechanism of the hydrogenolysis of cellulose into C$_2$/C$_3$ products, the reactions of the possible intermediates (such as glucose, fructose, sorbitol, mannitol, dihydroxyacetone and acetol) were performed, as shown in Table 2. As displayed in Entry 1, sorbitol and mannitol were stable and did not readily undergo further conversion$^{27,32,33}$, while glucose and fructose (Table 2, entries 3 and 5) were readily converted to EG and PG through hydrogenolysis, indicating that if the target products were C$_2$/C$_3$ glycols, when the loading of Ni was higher (e.g., 15Ni-20W, Fig. 3). Excess Ni promoted route 3 because sorbitol and mannitol were readily generated only through glucose hydrogenation$^{30,31}$. In summary, W worked on R2, while Ni acted on R3, and the favourability of routes 1, 2 or 3 was determined by the synergy of Ni and W. Based on the above mechanism, 7Ni-20W/β performed, as shown in Table 2. As displayed in Entry 1, sorbitol and mannitol were stable and did not readily converted to EG in a yield of 51% and PG in 14.5%, suggesting that route 1 is favoured over route 2 (Fig. 4). When the W loading was sufficient (e.g., 15Ni-20W, Fig. 3). Excess Ni promoted route 3 because sorbitol and mannitol were readily generated only through glucose hydrogenation$^{30,31}$. In summary, W worked on R2, while Ni acted on R3, and the favourability of routes 1, 2 or 3 was determined by the synergy of Ni and W. Based on the above mechanism, 7Ni-20W/β successfully drove the reaction through routes 1 and 2 and ultimately provided the maximum yield of C$_2$/C$_3$ glycols.

Reusability. Catalyst recycling is an important property for the practical application of catalysts in metal-catalysed liquid-phase reactions for the following two major reasons: 1) the catalyst can readily leach metal, which is attributed to the H$^+$ formed in water at high temperature$^{34,35}$, and 2) the complex intermediate compounds produced by the side reactions can block the pores and poison the catalyst$^{36,37}$. Therefore, the reusability of Ni-W-ZnO/β and the changes in its composition and structure were tested, and the results are displayed in Fig. 5, Table S2 and Table 3. As Fig. 5 shows, the yield of total glycols decreased from 70.1% to 68.1%, 64.8% and 59.7%
by the second, third and fourth runs, respectively, while the conversion of cellulose remained at 100%, 96% and 92%. The slight decrease could be attributed to structural changes, metal leaching from the catalyst and acidity decrease, which was verified by N2-adsorption and desorption (Table S2) and ICP results (Table 3) and NH3-TPD (Table S3), respectively. As shown by Table S2, entries 9 and 15–17, with the reuse of the catalyst, the BET surface area of Ni-W/β decreased slightly from 287 to 255 m²/g. It could be speculated that deposition of carbon species and collapse of the mesopores occurred during reuse, changing the catalytic structure. Nevertheless, differences between the pore volume and size in fresh and used catalysts were not significant, suggesting that the catalytic structure was not badly damaged by four cycles of reuse. As displayed in Table 3, the loading of Ni decreased from 7.29 to 6.41, 5.73, 5.64 and 5.58 wt% over four cycles of reuse, while W decreased from 20.87 to 18.11, 15.26, 13.58 and 11.56 wt%. As shown in Table S3 (Entries 4, 10–12), the acidity of the catalyst decreased during four cycles reaction, which may attributed to the leaching of Ni and W and the decreased BET surface area. What’s more, the increasing tendency of Ni/W weight ratio (from 0.35 to 0.41) suggested that the leaching W was faster than Ni, indicating the reaction route might be changed by the synergy of Ni and W. In the first and second cycles (Fresh and Reuse 1), the loadings of Ni and W were relatively balance. In this case, the high C2/C3 glycol yields (70.1% and 68.1%) could be attributed to the balance loading of Ni and W. In the third and fourth cycles (Reuse 2 and 3), the yield of C2/C3 glycols decreased to 64.8% and 59.7%, respectively, while the yields of mannitol and sorbitol were significantly increased. According to the above mechanism (Fig. 4), W promoted R2, while Ni promoted R3, and the favourability of routes 1, 2 or 3 was determined by the synergy of Ni and W. Take the fourth cycle (Reuse 3) as an example, the loading of W was insufficient because of the faster leaching of W than Ni. Therefore, R2 in routes 1 and 2 was disfavoured, while R3 in route 3 was favoured, which led to an increase in the mannitol and sorbitol yield and a decrease in EG and 1,2-PG. According to the above results and discussion, the loading of Ni and W and the balance of hydrogenation and RAC are also greatly important during reuse. What’s more, because of the leaching of Ni and W was obvious and could not be neglected, the effect of leached Ni and W on cellulose hydrogenolysis into PG/EG was investigated (Table S5). The results suggested that when the supported W was sufficient, the leached W did not work significantly on PG/EG production, while there was no supported W, the leached W could play a role in the reaction, which was the evidence that supported W, other than leached W, had a major role on PG/EG production in our catalytic system.

Figure 5. Reuse of the ZnO and Ni-W/β catalyst system. Reaction conditions: 30 min, 6 Mpa H2, 245 °C, 50 mL of H2O, 0.5 g of cellulose, 0.15 g of catalyst, and 100 mg of ZnO. EG: ethylene glycol; PG: 1,2-propylene glycol; S: sorbitol; and M: mannitol.

Table 3. Changes in the nickel, tungsten and zinc contents in the 7Ni-20W/β + ZnO system during four cycles of reuse. Liquid (wt% or %) = the weight of Ni, W or Zn in the liquid products after the reaction. The weight of Ni and W in the liquid products was converted into equivalent loadings in the catalyst (wt %). Solid (wt% or %) = the weight of Ni, W or Zn in the solid catalysts after the reaction. Ni, W or Zn balance (wt% or %) = the weight of Ni, W or Zn in the liquid products + the weight of Ni, W or Zn in the solid catalysts – the weight of Ni, W or Zn before the reaction.
Conclusion
To promote the selective transformation of cellulose into C2/C3 glycols and increase the proportion of C3 glycol in the glycol products, we attempted to control the synergy of the retro-aldol condensation, hydrogenation and isomerization reactions. After the optimization of the catalyst support, the Ni-W loading and the co-catalyst, ZnO-modified 7Ni-20W/β was employed, and the influence of these factors on the product distribution was discussed. Compared to supports such as Al2O3, TiO2, SiC and ZSM-5, raw β-zeolite exhibited the best catalytic performance, which was attributed to its ability to promote the hydrolysis of cellulose into small molecules by its abundant acid sites. The synergy of Ni and W was the key to the reaction: on the one hand, the synergy of Ni and W could provide both Lewis and Brønsted acid sites in the catalyst and sequentially promote the formation of C2/C3 glycols; on the other hand, Ni is effective in the hydrogenation, and W facilitates the bond cleavage (C6 to C2/C3). The optimum loadings of Ni and W were 7 wt% and 20 wt% because an unbalanced loading of Ni and W had a detrimental influence on the synergy of the hydrogenation and retro-aldol condensation. Moreover, with the leaching of the metals during four cycles of reuse, the catalytic performance was also influenced by the synergy of Ni and W primarily through the change in their loading. In addition, by screening a series of metal oxides and alkalis as co-catalysts in the Ni-W/β system, ZnO caused the greatest improvement in the C2/C3 yield. The increased yield of C3 glycol by ZnO was attributed to the promotion of the isomerization of glucose to fructose. After the systematic optimization of the catalyst support, the Ni-W loading and the co-catalyst, the yield of C2/C3 glycols reached 70.1%, with propylene glycol accounting for 51.1% of the product, under 4 MPa hydrogen pressure at 245 °C for 30 min.

Methods
Catalyst Preparation. Commercial H-β-zeolite (Catalyst Plant of Nankai University), denoted as “raw β”, was firstly dealuminated by refluxing in nitric acid at 80 °C at a solid-to-liquid ratio of 1 g: 20 mL under a stirring speed of 200 r/min for 20 h. After dealumination, denoted as “β”, the zeolite powder was collected by centrifugation and then washed with deionized water several times until the supernatant was neutral. Finally, the obtained β-zeolite was dried at 150 °C overnight.

The catalysts, including Ni-W/raw-β, Ni-W/β, Ni-W/Al2O3, Ni-W/SiC, Ni-W/ZSM-5 and Ni-W/TiO2, were prepared by incipient wetness impregnation, dried at 120 °C overnight, calcined at 500 °C for 4 h, and reduced under a hydrogen-nitrogen flow (volume ratio = 5%: 95%) at 500 °C for 4 h. In detail, the Ni-W/β catalysts were prepared by co-impregnation with an aqueous solution of ammonium metatungstate hydrate (AMT) and Ni(NO3)2·6H2O. Regarding the nickel and tungsten loadings, the nickel and tungsten loadings were 7 wt % and 20 wt %, respectively. All chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd.

Analytical methods. The specific surface area, pore volume and pore diameter of the catalysts were tested by N2 adsorption–desorption (Micromeritics ASAP 2020)60. Each sample was purged in a vacuum at 300 °C for 3 h before analysis. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface areas of the catalysts, the pore volume was calculated by the Barrett-Joyner-Halenda (BJH) model and the pore diameter was calculated by the BJH method from the desorption branches. Powder X-ray diffraction (XRD) patterns were collected on an X-ray powder diffractometer (Bruker D8 Advance) with Cu Kα radiation (40 kV, 40 mA) over a 2θ range of 5° to 80° at room temperature. Transmission electron microscopy (TEM) images were recorded on a JEOLJEM-1230 instrument operated at 80 kV.

The acidic properties of the catalysts were tested by NH3 temperature-programmed desorption (NH3-TPD) and pyridine infrared (Py-IR) spectroscopy24. The NH3-TPD was conducted using a Micromeritics AutoChemII 2920 system. The sample was pretreated in helium at 300 °C for 60 min, after which the sample was cooled to 120 °C in a helium flow. Next, 5% NH3 in the helium flow was absorbed onto the sample at 120 °C for 120 min. Finally, NH3-TPD was carried out under a hydrogen-nitrogen flow (volume ratio = 5%: 95%) at 500 °C for 4 h. The Py-IR spectra were recorded on a Perkin Elmer Frontier FT-IR in the range of 1400–1700 cm−1 with a spectral resolution of 2 cm−1. A 10-mg sample of catalyst was pressed into a wafer with a diameter of 13 mm and then set in a quartz IR cell. The catalysts were dried at 400 °C for 2 h under vacuum. After cooling, pyridine vapor was injected into the cell, and the adsorption period lasted for 30 min. Subsequently, the desorption profiles at 150 °C (1 h), 250 °C (1 h), 350 °C (1 h), and 400 °C (1 h) were recorded.

The confirmation of thorough dealumination in β, the metal loadings in the solid catalyst and the leaching of the metals into the liquid were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin Elmer Optima 2100 DV). Prior to the measurements, the solid samples were digested in an acidic mixture (HF:HNO3:HClO3 = 1:1:1), and the liquid samples were digested in HNO3 at 150 °C for 12 h.

Catalytic Reaction. The catalytic experiments were carried out in a 100-mL stainless steel autoclave with a Teflon insert, and the operating parameters were the same as those in our previous study40. To the autoclave were added 0.5 g of cellulose, 150 mg of catalyst, and 50 mL of water. Microcrystalline cellulose (Shanghai Chineway Pharm. Tech. Co. Ltd.) was dried under vacuum at 105 °C for 12 h before use. After the reactor was sealed, the vessel was purged with nitrogen three times to exclude air and then pressurized with 6 MPa of hydrogen and heated to the desired reaction temperature, which was kept constant throughout the reaction with stirring at 1000 rpm. The zero point of the “reaction time” was defined as the time point at which the required temperature was reached. When the reaction ended, the reactor was immediately quenched to room temperature in an ice-water bath. The products were quantified by gas chromatography (GC, Agilent 7820 A, J&W125–7332, 30 m × 530 μm × 1 μm) with an FID detector and high-performance liquid chromatography (HPLC, Agilent 1200, Shodex SUGAR SH1011) with VWD and RI detectors. The cellulose conversion (%) was determined from the change in the cellulose weight from before to after the reaction, and this value was further verified by
measuring the total organic carbon (TOC—VCPh, Shimadzu, Japan). The yield of products (%) was defined as

\[ \text{Yield} = \left( \frac{\text{weight of carbon in one product after reaction}}{\text{weight of carbon in cellulose before reaction}} \right) \times 100\% \]

For the catalyst reuse studies, the solid catalysts were collected by filtration and washed several times with water. The recovered catalysts were used after reduction in a mixed hydrogen-nitrogen flow (volume ratio = 5\%: 95\%) at 280 °C for 4 h to remove residual cellulose and keep Pt in its metallic state.

References

1. Binder, J. B. & Raines, R. T. Simple Chemical Transformation of Lignocellulosic Biomass into Furans for Fuels and Chemicals. J. Am. Chem. Soc. 131, 1979–1985 (2009).
2. Liu, C. Z., Qian, W. & Zhao, Z. K. Acid in ionic liquid: an efficient system for hydrolysis of lignocellulose. Green Chemistry 10, 177–182 (2008).
3. Dr, R. R., Dr, R. P. & Prof., F. S. & #x. Depolymerization of Cellulose Using Solid Catalysts in Ionic Liquids. Angew. Chem. Int. Ed. 47, 8047 (2008).
4. Yan, N. et al. One-step conversion of cellulose to C6-alcohols using a ruthenium nanocluster catalyst. J. Am. Chem. Soc. 128, 8714 (2006).
5. Fukuoka, A. & Dhepe, P. L. Catalytic conversion of cellulose into sugar alcohols. Angew. Chem. 45, 5161 (2006).
6. Sun, R. et al. Versatile Nickel–Lanthanum(III) Catalyst for Direct Conversion of Cellulose to Glycols. ACS Catalysis 5, 874–883 (2015).
7. Zheng, M., Pang, J., Sun, R., Wang, A. & Zhang, T. Selectivity Control for Cellulose to Diols: Dancing on Eggs. ACS Catalysis 7, 1939–1954, https://doi.org/10.1021/acscatal.6b03469 (2017).
8. Ji, N. et al. Direct catalytic conversion of cellulose into ethylene glycol using nickel-promoted tungsten carbide catalysts. Angew. Chem. 47, 8510 (2008).
9. Zhao, G., Zheng, M., Wang, A. & Tao, Z. Catalytic Conversion of Cellulose to Ethylene Glycol over Tungsten Phosphide Catalysts. Chinese Journal of Catalysis 31, 928–932 (2010).
10. Zhu, M. et al. Transition metal-tungsten bimetallic catalysts for the conversion of cellulose into ethylene glycol. ChemSusChem 3, 63–66 (2010).
11. Liu, Y., Luo, C. & Liu, H. Tungsten trioxide promoted selective conversion of cellulose to propylene glycol and ethylene glycol on a ruthenium catalyst. Angew. Chem. 51, 3249 (2012).
12. Tai, Z., Zhang, J., Wang, A. & Zheng, M. Temperature-controlled phase-transfer catalysis for ethylene glycol production from cellulose. Chem. Commun. 48, 7052 (2012).
13. Xiao, Z., Jin, S., Pang, M. & Liang, C. Conversion of highly concentrated cellulose to 1,2-propanediol and ethylene glycol over highly efficient CuCr catalysts. Green Chemistry 15, 891–895 (2013).
14. Deng, T. Y. & Liu, H. C. Promoting effect of SnOx on selective conversion of cellulose to polyols over bimetallic Pt-SnOx/Al2O3 catalysts. Green Chemistry 15, 116–124 (2012).
15. Sun, R. et al. Selectivity-switchable conversion of cellulose to glycols over Ni-Sn catalysts. ACS Catalysis 6 (2016).
16. Xi, J. et al. Production of Ethylene Glycol and Its Monoether Derivative from Cellulose. ACS Sustainable Chemistry & Engineering 2, 2355–2362 (2014).
17. Wang, X. et al. Efficient conversion of microcrystalline cellulose to 1,2-alkanediols over supported Ni catalysts. Green Chemistry 14, 758–765 (2012).
18. Deng, T. & Liu, H. Direct conversion of cellulose into acetol on bimetallic Ni-SnOx/Al2O3 catalysts. Journal of Molecular Catalysis A Chemical 388–389, 66–73 (2014).
19. Dong, W. et al. Selective Chemical Conversion of Sugars in Aqueous Solutions without Alkali to Lactic Acid Over a Zn-Sn-Beta Lewis Acid-Base Catalyst. Scientific Reports 6, 26713 (2016).
20. Xia, M. et al. Synergetic effects of bimetal in modified beta zeolite for lactic acid synthesis from biomass-derived carbohydrates. Rsc Advances 8, 8965–8973, https://doi.org/10.1039/C8RA12333G (2018).
21. Liu, C. et al. Effect of WOx on Bifunctional Pd-WOx/Al2O3 Catalysts for the Selective Hydrogenolysis of Glucose to 1,2-Propanediol. ACS Catalysis 5, 4612–4623, https://doi.org/10.1021/acscatal.5b00800 (2015).
22. Liu, C. et al. WOx modified Cu/Al2O3 as a high-performance catalyst for the hydrogenolysis of glucose to 1,2-propanediol. Catal. Today 261, 116–127, https://doi.org/10.1016/j.cattod.2015.06.030 (2016).
23. Zheng, M. Y. et al. Transition metal–tungsten bimetallic catalysts for the conversion of cellulose into ethylene glycol. ChemSusChem 3, 63–66 (2010).
24. Lazaridis, P. A. et al. High hexitols selectivity in cellulose hydrolytic hydrogenation over platinum (Pt) vs. ruthenium (Ru) catalysts supported on micro/mesoporous carbon. Applied Catalysis B:Environmental 214, 1–14, https://doi.org/10.1016/j.apcatb.2017.05.031 (2017).
25. Dong, W. et al. Selective Chemical Conversion of Sugars in Aqueous Solutions without Alkali to Lactic Acid Over a Zn-Sn-Beta Lewis Acid-Base Catalyst. Scientific Reports 6, 26713 (2016).
26. Girard, E., Delcroix, D. & Cabiac, A. Catalytic conversion of cellulose to C2–C3 glycols by dual association of a homogeneous metallic salt and a perovskite-supported platinum catalyst. Catalysis Science & Technology 6 (2016).
27. Hirano, Y., Sagata, K. & Kita, Y. Selective transformation of glucose into propylene glycol on Ru/C catalysts combined with ZnO under low hydrogen pressures. Applied Catalysis A: General 492, 1–7 (2015).
28. Hirano, Y., Sagata, K. & Kita, Y. Selective transformation of glucose into propylene glycol on Ru/C catalysts combined with ZnO under low hydrogen pressures. Applied Catalysis A General 502, 1–7 (2015).
29. Liu, C. et al. Effect of WOx on Bifunctional Pd–WOx/Al2O3 Catalysts for the Selective Hydrogenolysis of Glucose to 1,2-Propanediol. ACS Catalysis 5, 4612–4623 (2015).
30. Ooms, K. et al. Conversion of sugars to ethylene glycol with nickel–tungsten carbide in a fed-batch reactor: high productivity and reaction network elucidation. Green Chemistry 16, 695–707 (2014).
31. Cao, Y., Wang, J., Kang, M. & Zhu, Y. Catalytic conversion of glucose and cellulose to ethylene glycol over Ni–WO3/SBA-15 catalysts. RSC Advances 5, 90904–90912 (2015).
32. Liu, Y., Luo, C. & Liu, H. Tungsten trioxide promoted selective conversion of cellulose into propylene glycol and ethylene glycol on a ruthenium catalyst. Angewandte Chemie 124, 3303–3307 (2012).
33. Zhou, L., Wang, A., Li, C., Zheng, M. & Zhang, T. Selective Production of 1,2-Propylene Glycol from Jerusalem Artichoke Tubers using Ni–W/C catalysts. ChemSusChem 5, 932–938 (2012).
34. Kobayashi, H. et al. Synthesis of sugar alcohols by hydrolytic hydrogenation of cellulose over supported metal catalysts. Green Chemistry 13, 326–333 (2011).
35. Guo, X. et al. Co/MgO catalysts for hydrogenolysis of glycerol to 1,2-propanediol. Applied Catalysis A: General 371, 108–113 (2009).
36. Rinaldi, R. & Schüth, F. Design of solid catalysts for the conversion of biomass. Energy & Environmental Science 2, 610–626 (2009).
37. Galliez, P., Cerino, P., Blanc, B., Fleche, G. & Fuertes, P. Glucose hydrogenation on promoted raney-nickel catalysts. Journal of Catalysis 146, 93–102 (1994).
38. Wang, F.-F. et al. Conversion of cellulose to lactic acid catalyzed by erbium-exchanged montmorillonite K10. Green Chem. 17, 2455–2463, https://doi.org/10.1039/c4gc02131b (2015).
39. Dijkmans, J. et al. Productive sugar isomerization with highly active Sn in dealuminated β zeolites. Green Chemistry 15, 2777–2785 (2013).
40. Gu, M. et al. The Effect of Catalytic Structure-modification on Hydrogenolysis of Glycerol into 1,3-propanediol over Platinum Nanoparticles and Ordered Mesoporous Alumina Assembled Catalysts. Industrial & Engineering Chemistry Research 56 (2017).
41. Emeis, C. A. Determination of Integrated Molar Extinction Coefficients for Infrared Absorption Bands of Pyridine Adsorbed on Solid Acid Catalysts. Cheminfor 24, no–no (1993).
42. Kilzer, F. J. & Broido, A. Speculations on the nature of cellulose pyrolysis. Pyrodynamics. 2, 151–163 (1965).

Acknowledgements
The authors acknowledge sponsorship of the National Natural Science Foundation of China (No. 21676205), the National Science Fund for Distinguished Young Scholars (No. 51625804), the National Key R&D Program of China (No. 2018YFD1100503) and the Fundamental Research Funds for the Central Universities (No. 22120190012, 22120190054).

Author Contributions
Minyan Gu, Zheng Shen and Yalei Zhang conceived the idea and designed the experiments. Minyan Gu and Long Yang did the experiments and wrote the paper. Wenjie Dong, Ling Kong, Wei Zhang and Boyu Peng modified the paper. Yalei Zhang and Zheng Shen supervised the whole work.

Additional Information
Supplementary information accompanies this paper at https://doi.org/10.1038/s41598-019-48103-6.

Competing Interests: The authors declare no competing interests.

Publisher’s note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.

© The Author(s) 2019