

# One Pot Synthesis of Bio-Ethylene Glycol from Cellulose

Yu-Wen Chen\*, Der-Shing Lee

Department of Chemical and Materials Engineering, National Central University, Taipei City

Email: \*ywchen@cc.ncu.edu.tw

**How to cite this paper:** Chen, Y.-W. and Lee, D.-S. (2021) One Pot Synthesis of Bio-Ethylene Glycol from Cellulose. *Modern Research in Catalysis*, 10, 93-101. <https://doi.org/10.4236/mrc.2021.104006>

**Received:** September 4, 2021

**Accepted:** October 24, 2021

**Published:** October 27, 2021

Copyright © 2021 by author(s) and Scientific Research Publishing Inc.

This work is licensed under the Creative Commons Attribution International License (CC BY 4.0).

<http://creativecommons.org/licenses/by/4.0/>



Open Access

## Abstract

In this study, various composite Ni-W<sub>2</sub>C/active carbon catalysts were synthesized. W<sub>2</sub>C was prepared by carbothermal hydrogen reduction. The metal loading of W<sub>2</sub>C in catalyst was 30 wt.%. Carbon was impregnated with metatungstate. It was dried at 120°C for 12 h. Carbon was then carburized in H<sub>2</sub> flow, the temperature was increased from 25°C to 450°C, and then to 800°C and stayed for 4 h. The W<sub>2</sub>C/active carbon was treated with H<sub>2</sub>SO<sub>4</sub> to create more function groups on the surface. Ni-W<sub>2</sub>C/active carbon was prepared by incipient-wetness impregnation method. After calcination and reduction processes in H<sub>2</sub> flow, Ni-W<sub>2</sub>C/active carbon catalyst was obtained. The reaction of cellulose to ethylene glycol in one step was carried out in a batch reactor under the following condition: 1 g cellulose, 0.3 g catalyst, 100 ml H<sub>2</sub>O, 4 - 6 MPa H<sub>2</sub>, 220°C - 280°C, and 400 rpm. The reaction between cellulose and catalyst is a solid-solid reaction; therefore, the contact between these two solid materials is important. Long ball milling time would increase the contact between these two solids. The ball milling time and the functional groups on active carbon play important roles in this reaction. The results demonstrated that one pot synthesis of EG from cellulose is economically and technically feasible.

## Keywords

Bio Ethylene Glycol, Cellulose Conversion, NiW<sub>2</sub>C/Carbon

## 1. Introduction

Ethylene glycol (EG) is a large bulk polyol. It is widely used in the synthesis of polyester. Many big companies such as Coca Cola and Pepsi have asked their vendors to use bio EG. The conversion of cellulose directly to EG in one step is an important technology. Many companies in the world are eager to develop this

process [1]-[12]. Since the first disclosure in 2008, the one-pot catalytic conversion of cellulose to EG has gained remarkable advances in scientific understanding and industrial application [12]-[17]. Catalyst and reaction conditions are the key in this process. Many researchers have reported that Ni-W<sub>2</sub>C/carbon is a good catalyst for this reaction [1]-[17]. Kandasamy *et al.* [1] gave a very excellent review on this reaction. Wang and Zhang [2] reported to use multifunctional tungsten-based catalysts for one-pot conversion to convert cellulose to ethylene glycol. Xin *et al.* [3] reported that bimetal oxide catalyst including tungsten oxide is a good catalyst to have high selectivity to ethylene glycol. Molder *et al.* [4] reported the influence of lignin on the yield of ethylene glycol. Yu *et al.* [5] showed the synergistic Effect of Ni/W/Cu on MgAl<sub>2</sub>O<sub>4</sub> for this reaction at a low H<sub>2</sub> pressure. Li *et al.* [6] reported that Ni/W/Ti is a good catalyst for this reaction and Ti-O-W linkage is beneficial for the stability of the catalyst. Sun *et al.* [12] reported that nickel-lanthanum oxide catalyst is a good catalyst for this reaction. Yu *et al.* [15] shows the reaction network and mechanism for this reaction over NiO<sub>x</sub>-WO<sub>y</sub>-Cu/MgAl<sub>2</sub>O<sub>4</sub> catalyst. However, there is still a room to improve the yield of EG. By changing the method of ball milling, reduction method, and Ni and W<sub>2</sub>C contents, one can improve the conversion of cellulose and selectivity of EG. The aim of this study was to develop an optimum one-pot process from cellulose to EG.

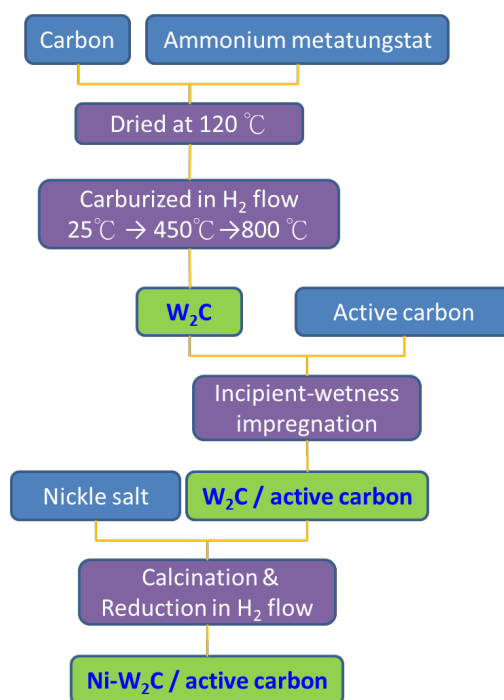
In this study, various composite Ni-W<sub>2</sub>C/active carbon catalysts were synthesized by using different preparation methods. W<sub>2</sub>C was prepared by carbothermal hydrogen reduction. Carbon was impregnated with metatungstate. Ni(NO<sub>3</sub>)<sub>2</sub> solution was added on W<sub>2</sub>C/carbon by incipient-wetness impregnation method. The reaction was carried out in a Parr reactor. Various preparation parameters and reaction parameters were investigated in this study.

## 2. Experimental

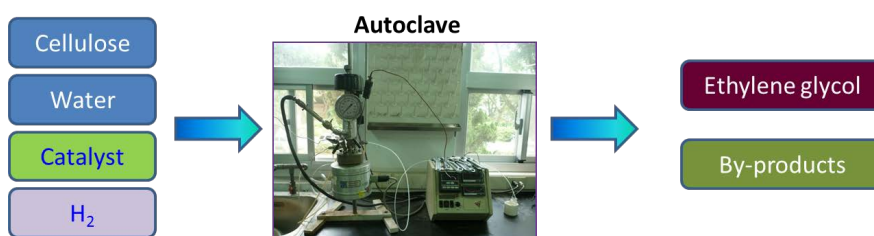
Various composite Ni-W<sub>2</sub>C/active carbon catalysts were synthesized by using different preparation methods. W<sub>2</sub>C was prepared by carbothermal hydrogen reduction. The metal loading of W<sub>2</sub>C in catalyst was 30 wt.%. Carbon was impregnated with metatungstate. It was dried at 120°C for 12 h. Carbon was then carburized in H<sub>2</sub> flow, the temperature was increased from 25°C to 450°C, and then to 800°C and stayed for 4 h. The W<sub>2</sub>C/active carbon was treated with H<sub>2</sub>SO<sub>4</sub> to create more function groups on the surface. Ni(NO<sub>3</sub>)<sub>2</sub> aqueous solution was added in W<sub>2</sub>C/active carbon by incipient-wetness impregnation method. After calcination and reduction processes in H<sub>2</sub> flow, Ni-W<sub>2</sub>C/active carbon catalyst was obtained. The catalyst preparation method is depicted in **Figure 1**.

The catalysts were characterized by N<sub>2</sub> sorption. The bulk surface area was calculated by BET method, and the pore size distribution was obtained by BJH method. Transmission electron microscopy (JSM-F200) was used to investigate the morphology of the catalysts.

The reaction was carried out in a Parr reactor as shown in **Figure 2**. The



**Figure 1.** The catalyst preparation method.



**Figure 2.** Reaction setup.

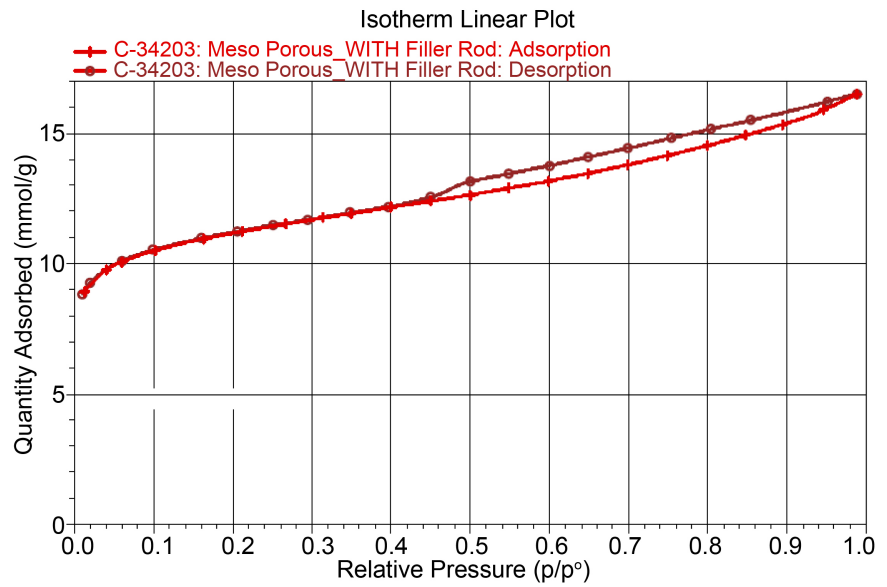
reaction condition was 1 g cellulose, 0.3 g catalyst, 100 ml H<sub>2</sub>O, 4 - 6 MPa H<sub>2</sub>, 220 °C - 280 °C, and 400 rpm. Before reaction, cellulose and catalyst were grounded by ball mill for several hours.

### 3. Results and Discussion

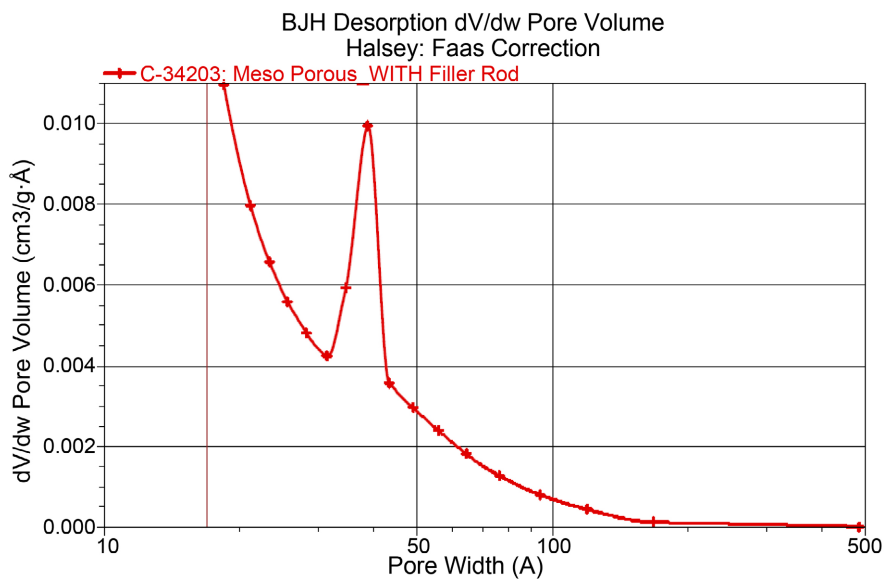
N<sub>2</sub> adsorption-desorption isotherms of the catalyst are shown in **Figure 3**. It shows that the major adsorption was in the nanopore range. The pore size distribution of the catalyst by BJH method is shown in **Figure 4**. The main peak diameter is 3.5 nm.

The TEM image of the Ni-W<sub>2</sub>C/carbon catalyst is shown in **Figure 5**. It shows that the catalysts had particle size around 30 nm.

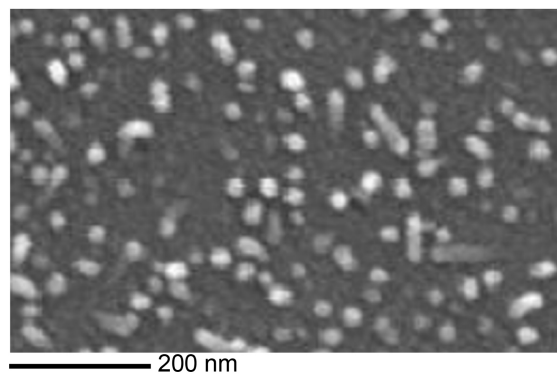
The reaction results on different catalysts are displayed in **Figure 6**. The conversion of cellulose and EG yield increased in the order of Ni/active carbon < W<sub>2</sub>C/active carbon < NiW<sub>2</sub>C/carbon. High cellulose conversion and high selectivity to ethylene glycol was obtained on NiW<sub>2</sub>C/active carbon catalyst. The sulfonated activated carbon has many functional groups on the surface of carbon. It



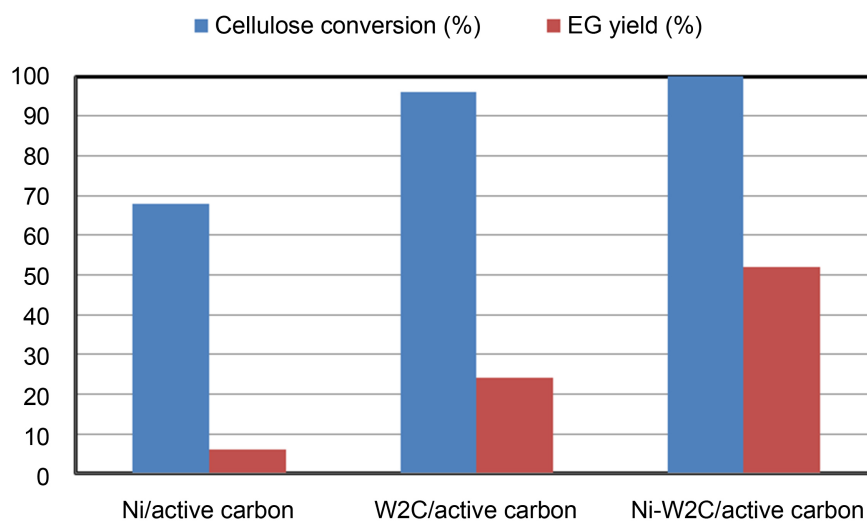
**Figure 3.** N<sub>2</sub> adsorption-desorption isotherm of the Ni-W<sub>2</sub>C/carbon catalyst.



**Figure 4.** Pore size distribution of the Ni-W<sub>2</sub>C/carbon catalyst.



**Figure 5.** SEM image of the Ni-W<sub>2</sub>C/carbon catalyst.



**Figure 6.** Effect of catalyst on the catalytic reaction of cellulose to EG. (Reaction condition: 1 g cellulose, 0.3 g catalyst, 100 ml H<sub>2</sub>O, 6 MPa H<sub>2</sub>, 250 °C, reaction time 60 min, 400 rpm)

is believed that cellulose was converted to glucose on carbon, and then converted to EG on Ni-W<sub>2</sub>C via hydrogenolysis reaction.

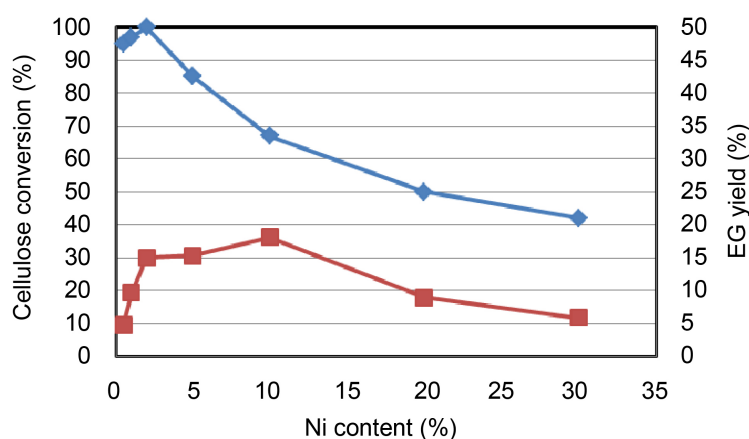
The effect of Ni content in Ni-W<sub>2</sub>C/active carbon on the catalytic reaction of cellulose to EG is listed in **Table 1**. The maximum cellulose conversion was obtained for 2% Ni content on W<sub>2</sub>C/active carbon, but the optimal EG selectivity was in the catalyst with 10% Ni content. As mentioned above, the hydrolysis of cellulose is occurred on the interaction of cellulose and active carbon. Therefore long ball milling time would increase the contact between cellulose and active carbon. However, the hydrogenolysis reaction of glucose to EG is mainly contributed to Ni-W<sub>2</sub>C catalyst. Therefore, high Ni loading will cover the surface of carbon, block the functional groups on the surface of carbon, and decreased the conversion of cellulose. Adequate Ni loading can enhance the hydrogenolysis reaction and increasing the EG selectivity.

The effects of Ni loading on the cellulose conversion and EG yield are shown in **Figure 7**. The conversion of cellulose increased with an increase in Ni content at low metal loading range and reached 100% conversion at 2 wt.% Ni. It then decreased with increase of Ni content. It should be noted that when Ni loading increased, the W<sub>2</sub>C content decreased. The EG yield followed the similar trend as cellulose conversion. It infers that the cellulose conversion is dependent on the W<sub>2</sub>C content.

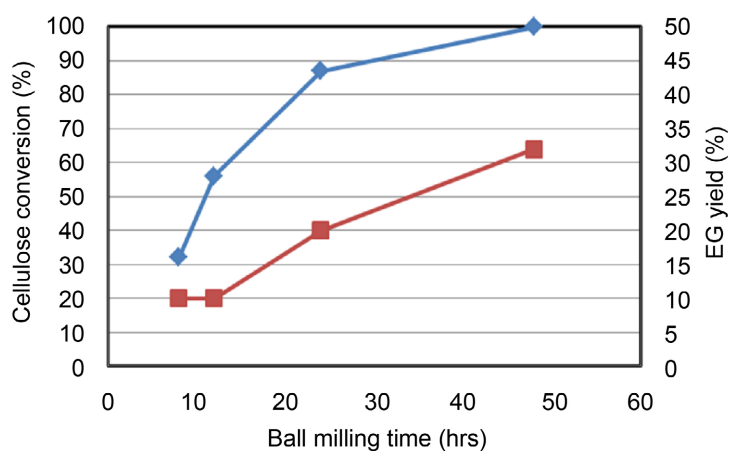
The reaction between cellulose and catalyst is a solid-solid reaction; therefore the contact between these two solid materials is important. **Figure 8** shows that the longer ball milling time is, the higher cellulose conversion and EG yield are. The results show that the ball milling time and the amount of functional groups on active carbon play important roles in this reaction. Water is a good solvent. At room temperature, cellulose is not dissolved in water. At high temperature, cellulose can dissolve in water. The ionic product of water at 250 °C is 100 times

**Table 1.** Effect of Ni content in Ni-W<sub>2</sub>C/active carbon on the catalytic reaction of cellulose to EG. (Reaction condition: 1 g cellulose, 0.3 g catalyst, 100 ml H<sub>2</sub>O, 4 MPa H<sub>2</sub>, 250 °C, 60 min, reaction time, 400 rpm).

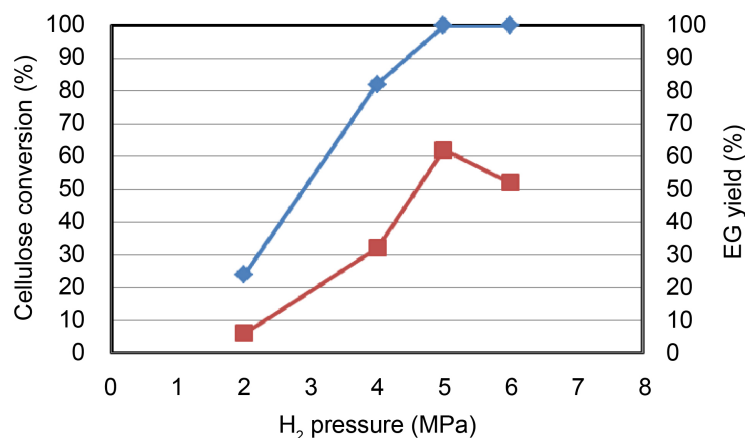
Ni content (%)	Cellulose conversion (%)	EG selectivity (%)	Hexahydric alcohol selectivity (%)	Others (%)
0.5	95	5	3	92
1	97	10	5	85
2	100	15	6	79
5	85	18	8	74
10	67	27	12	61
20	50	18	14	68
30	42	14	17	69



**Figure 7.** Effect of Ni content in Ni-W<sub>2</sub>C/active carbon on the catalytic reaction of cellulose to ethylene glycol. (Reaction condition: 1 g cellulose, 0.3 g catalyst, 100 ml H<sub>2</sub>O, 4 MPa H<sub>2</sub>, 250 °C, reaction time 60 min, 400 rpm.) blue color: cellulose conversion; red color: EG yield.



**Figure 8.** Effect of ball milling time in Ni-W<sub>2</sub>C/active carbon on the catalytic reaction of cellulose to EG. (Reaction condition: 1 g cellulose, 0.3 g catalyst, 100 ml H<sub>2</sub>O, 4 MPa H<sub>2</sub>, 250 °C, reaction time 60 min, 400 rpm.) blue color: cellulose conversion; red color: EG yield.



**Figure 9.** Effect of H<sub>2</sub> pressure in 2% Ni-W<sub>2</sub>C/active carbon on the catalytic reaction of cellulose to ethylene glycol. (Reaction condition: 1 g cellulose, 0.3 g catalyst, 100 ml H<sub>2</sub>O, 250 °C, reaction time 60 min, 400 rpm, blue color: cellulose conversion; red color: EG yield)

of that at room temperature.

**Figure 9** shows the effect of hydrogen pressure on the cellulose conversion and EG yield. Cellulose conversion increased with an increase of hydrogen pressure. EG yield shows the same trend. As the hydrogen pressure reached 6 MPa, cellulose conversion reached 100%, but the selectivity of EG decreased, resulting in the decrease in EG yield.

#### 4. Conclusions

In this study, various composite Ni-W<sub>2</sub>C/active carbon catalysts were synthesized by using different preparation methods. W<sub>2</sub>C was prepared by carbothermal hydrogen reduction. The metal loading of W<sub>2</sub>C in catalyst was 30 wt%. Carbon was impregnated with metatungstate. It was dried at 120 °C for 12 h. Carbon was then carburized in H<sub>2</sub> flow, the temperature was increased from 25 to 450 °C, and then to 800 °C and stayed for 4 h. Ni(NO<sub>3</sub>)<sub>2</sub> solution was added on W<sub>2</sub>C/carbon by incipient-wetness impregnation method. The reaction was carried out in a Parr reactor under the following condition: 1 g cellulose, 0.3 g catalyst, 100 ml H<sub>2</sub>O, 4 - 6 MPa H<sub>2</sub>, 220 °C - 280 °C, and 400 rpm. Before reaction, cellulose and catalyst should be grounded by ball mill for several hours. High cellulose conversion and high selectivity to ethylene glycol was obtained by using sulfonated activated carbon, which has many function groups on the surface. It is concluded that cellulose was converted to glucose on carbon, and then converted to ethylene glycol on Ni-W<sub>2</sub>C by hydrogenolysis reaction.

#### Acknowledgements

Financial support was provided by Ministry of Science and Technology, Taiwan.

#### Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

## References

- [1] Kandasamy, S., Samudrala, S.P. and Bhattacharya, S. (2019) The Route towards Sustainable Production of Ethylene Glycol from a Renewable Resource, Biodiesel Waste: A Review. *Catalysis Science & Technology*, **9**, 567-577. <https://doi.org/10.1039/C8CY02035C>
- [2] Wang, A. and Zhang, T. (2013) One-Pot Conversion of Cellulose to Ethylene Glycol with Multifunctional Tungsten-Based Catalysts. *Accounts of Chemical Research*, **46**, 1377-1386. <https://doi.org/10.1021/ar3002156>
- [3] Xin, Q., Jiang, L., Yu, S., Liu, S., Yin, D., Li, L., Xie, C., Wu, Q., Yu, H., Liu, Y. and Liu, Y. (2021) Bimetal Oxide Catalysts Selectively Catalyze Cellulose to Ethylene Glycol. *The Journal of Physical Chemistry C*, **125**, 18170-18179. <https://doi.org/10.1021/acs.jpcc.1c04446>
- [4] Molder, T.D.J., Kersten, S.R.A., Lange, J.P. and Ruiz, M.P. (2021) Ethylene Glycol from Lignocellulosic Biomass: Impact of Lignin on Catalytic Hydrogenolysis. *Industrial & Engineering Chemistry Research*, **60**, 7043-7049. <https://doi.org/10.1021/acs.iecr.1c01063>
- [5] Yu, J., Liang, J., Chen, X., Wang, L., Wei, X., Li, Y. and Qin, Y. (2021) Synergistic Effect of Ni/W/Cu on MgAl<sub>2</sub>O<sub>4</sub> for One-Pot Hydrogenolysis of Cellulose to Ethylene Glycol at a Low H<sub>2</sub> Pressure. *ACS Omega*, **6**, 11650-11659. <https://doi.org/10.1021/acsomega.1c00979>
- [6] Li, N., Liu, X., Zhou, J., Ma, Q., Liu, M. and Chen, W. (2020) Enhanced Ni/W/Ti Catalyst Stability from Ti-O-W Linkage for Effective Conversion of Cellulose into Ethylene Glycol. *ACS Sustainable Chemistry & Engineering*, **8**, 9650-9659. <https://doi.org/10.1021/acssuschemeng.0c00836>
- [7] Zhang, K., Yang, G., Lyu, G., Jia, Z., Lucia, L.A. and Chen, J. (2019) One-Pot Solvothermal Synthesis of Graphene Nanocomposites for Catalytic Conversion of Cellulose to Ethylene Glycol. *ACS Sustainable Chemistry & Engineering*, **7**, 11110-11117. <https://doi.org/10.1021/acssuschemeng.9b00006>
- [8] Pang, J., Zheng, M., Li, X., Sebastian, J., Jiang, Y., Zhao, Y., Wang, A. and Zhang, T. (2019) Unlock the Compact Structure of Lignocellulosic Biomass by Mild Ball Milling for Ethylene Glycol Production. *ACS Sustainable Chemistry & Engineering*, **7**, 679-687. <https://doi.org/10.1021/acssuschemeng.8b04262>
- [9] Zheng, M., Pang, J., Sun, R., Wang, A. and Zhang, T. (2017) Selectivity Control for Cellulose to Diols: Dancing on Eggs. *ACS Catalysis*, **7**, 1939-1954. <https://doi.org/10.1021/acscatal.6b03469>
- [10] Sun, R., Zheng, M., Pang, J., Liu, X., Wang, J., Pan, X., Wang, A., Wang, X. and Zhang, T. (2016) Selectivity-Switchable Conversion of Cellulose to Glycols over Ni-Sn Catalysts. *ACS Catalysis*, **6**, 191-201. <https://doi.org/10.1021/acscatal.5b01807>
- [11] Li, C., Zhao, X., Wang, A., Huber, G.W. and Zhang, T. (2015) Catalytic Transformation of Lignin for the Production of Chemicals and Fuels. *Chemical Reviews*, **115**, 11559-11624. <https://doi.org/10.1021/acs.chemrev.5b00155>
- [12] Sun, R., Wang, T., Zheng, M., Deng, W., Pang, J., Wang, A., Wang, X. and Zhang, T. (2015) Versatile Nickel-Lanthanum(III) Catalyst for Direct Conversion of Cellulose to Glycols. *ACS Catalysis*, **5**, 874-883. <https://doi.org/10.1021/cs501372m>
- [13] Zhao, G., Zheng, M., Zhang, J., Wang, A. and Zhang, T. (2013) Catalytic Conversion of Concentrated Glucose to Ethylene Glycol with Semicontinuous Reaction System. *Industrial & Engineering Chemistry Research*, **52**, 9566-9572. <https://doi.org/10.1021/ie400989a>



- 
- [14] Mankar, A.R., Modak, A. and Pant, K.K. (2021) High Yield Synthesis of Hexitols and Ethylene Glycol through One-Pot Hydrolytic Hydrogenation of Cellulose. *Fuel Processing Technology*, **218**, Article ID: 106847. <https://doi.org/10.1016/j.fuproc.2021.106847>
- [15] Yu, J., Liang, J., Chen, X., Wang, L., Wei, X., Qin, Y., Li, Y. and Ling, Y. (2021) Reaction Network and Kinetics for the One-Pot Hydrogenolysis of Cellulose to Ethylene Glycol over NiO<sub>x</sub>-W<sub>o<sub>y</sub></sub>-Cu/MgAl<sub>2</sub>O<sub>4</sub>. *Reaction Kinetics, Mechanisms and Catalysis*, **133**, 55-71. <https://doi.org/10.1007/s11144-021-01975-0>
- [16] Pang, J., Zhang, B., Jiang, Y., Zhao, Y., Li, C., Zheng, M. and Zhang, T. (2021) Complete Conversion of Lignocellulosic Biomass to Mixed Organic Acids and Ethylene Glycol via Cascade Steps. *Green Chemistry*, **23**, 2427-2436. <https://doi.org/10.1039/D1GC00060H>
- [17] Ribeiro, L.S., Órfão, J.J.M. and Pereira, M.F.R. (2021) An Overview of the Hydrolytic Hydrogenation of Lignocellulosic Biomass Using Carbon-Supported Metal Catalysts. *Materials Today Sustainability*, **11-12**, Article ID: 100058. <https://doi.org/10.1016/j.mtsust.2020.100058>