

## Use of Single Atom Catalysis for Improvement of Lignocellulosic Conversion

Dian Cao, Bojin Zhang, Maolin Yang, Fang Luo, Xiaojun Yang, and Shengdong Zhu \*

Economical and efficient transformation of lignocellulosic biomass into fuels, chemicals, and materials has drawn much attention in recent years. Catalytic chemical conversion is one of the most widely used technical ways in lignocellulosic transformation because of its high efficiency. However, the traditional chemical conversion is often carried out at high temperatures and large amounts of byproducts are formed during the conversion process. This is due in part because the used catalyst has low activity, selectivity, and stability. This causes the traditional chemical conversion process to have a high cost and to encounter difficulty in industrialization. The single atom catalysis approach provides a promising solution to improve the traditional chemical conversion process and decrease its process cost. Compared with the traditional catalyst, the single atom catalyst has not only lower cost but also higher activity, selectivity, and stability. It is becoming a new frontier in lignocellulosic conversion. This editorial will give a brief discussion about opportunities and challenges of using single atom catalysis for improvement of the lignocellulosic conversion.

*Keywords: Single atom catalysis; Lignocellulosic biomass; Chemical conversion*

*Contact information: Key Laboratory for Green Chemical Process of Ministry of Education, Hubei Key Laboratory of Novel Chemical Reactor and Green Chemical Technology, School of Chemical Engineering and Pharmacy, Wuhan Institute of Technology, Wuhan 430073, PR China;*

*\* Corresponding author: whictzhusd@sina.com; zhusd2003@21cn.com*

### Technical Bottleneck for the Economical and Efficient Conversion of Lignocellulosic Biomass

Lignocellulosic biomass is the most abundant and renewable resource in the world. It is an attractive feedstock for the production of fuels, chemicals, and materials. As energy demands increase along with environmental concerns, there has been high interest in the production of fuels, chemicals, and materials from lignocellulosic biomass (Chen *et al.* 2014; Zhu *et al.* 2015a,b). The economical and efficient transformation of lignocellulosic biomass into fuels, chemicals, and materials is extremely important in maintaining the sustainable development of our society (Zhu *et al.* 2016, 2017). There are two ways to transform lignocellulosic biomass into fuels, chemicals, and materials. One is the fermentation process, and the other is chemical transformation (Ding *et al.* 2012). The fermentation process can be performed under relatively mild conditions, but it always has low transformation rate and efficiency. Before its fermentation, lignocellulosic biomass often needs to be pretreated and hydrolyzed to fermentable sugars. After the fermentation, the separation process is generally complicated and energy intensive because it has low product concentration. The production of ethanol from lignocellulosic biomass is the most typical process through a fermentation pathway

(Wang *et al.* 2018; Zhu *et al.* 2018). The complicated process, low transformation rate, and low efficiency limit the industrialization of fermentation process for lignocellulosic transformation. In contrast with the fermentation process, the chemical transformation always has high reaction rate and transformation efficiency. It also has a relatively simple process, because the pretreatment step is not needed for most chemical transform. These advantages have allowed the chemical transformation to become an active research area for lignocellulosic utilization (Yang *et al.* 2017). However, the traditional chemical conversion needs to be carried out at high temperatures and pressures, which increases the equipment investment and operation cost (Du *et al.* 2015; Chen *et al.* 2017). Because of the low selectivity of traditional catalysts, large amounts of byproducts will be formed during the traditional chemical transformation, which makes the separation of the targeted products difficult. Meanwhile, the traditional catalysts always have low stability under practical reaction conditions. In some traditional chemical transformation processes, noble metal catalysts are needed, which make it an expensive process (Zhang *et al.* 2015; Qin *et al.* 2017). All these disadvantages limit the chemical transformation used in practice. Therefore, development of new catalysts with low cost, high activity, selectivity, and stability is the technical key for the chemical conversion of lignocellulosic biomass.

### **Use of the Single Atom Catalysis for the Catalytic Chemical Conversion of Lignocellulosic Biomass**

The term single atom catalysts (SACs) refers to catalysts with individual and isolated metal atoms anchored to supports. SACs can act as the catalytic active centers. Single atom catalysis has garnered high interest because the process has resulted in significant cost reduction, high activity, selectivity, and stability (Kyriakou *et al.* 2012). Compared with the traditional catalysts, the SACs, especially for the noble metal catalysts, have lower cost because the active metals are highly dispersed and isolated single atoms on the support surface. Their higher activity and stability come from the strong interaction between the active metal atoms and the supports. Their higher selectivity is from their single catalytic active sites. Since first reported in 2011, studies on SACs have made great progress. To date, there are a large number of reports that show SACs can be used for a variety of important chemical reactions, such as oxidation, water gas shift, and hydrogenation (Kyriakou *et al.* 2012; Cao *et al.* 2017; Liu *et al.* 2017, 2018). Because of their fascinating performance, SACs have been widely used in such areas as energy, environment, and green synthesis, including the chemical transformation of lignocellulosic biomass into fuels, chemicals, and materials. They are emerging as a new frontier in lignocellulosic transformation. It is reported that Liu *et al.* (2018) developed a hydrothermally stable and acid resistant Ni-N-C SAC that performed very well in one-pot conversion of cellulose to ethylene glycolate. Compared to the conventional Ni/AC catalysis, the Ni-N-C SAC demonstrated superior activity and stability. It could be reused seven times without any deactivation, while the conventional Ni/AC catalyst had lost half of its initial activity during the 2<sup>nd</sup> run. Liu *et al.* (2017) reported another example using the Co-MoS<sub>2</sub> SAC for conversion of the oxygen-rich biomass into hydrocarbon fuels, especially for lignin transformation (Liu *et al.* 2017). In comparison with the traditional Co/MoS<sub>2</sub> catalyst, the Co-MoS<sub>2</sub> SAC exhibited superior activity, selectivity, and stability for the hydrodeoxygenation of 4-methylphenol to toluene,

which is a model reaction for lignin conversion. Because of its high activity, the reaction temperature could be decreased from the typically used 300 °C to 180 °C. Meantime, its activity and selectivity remained unchanged after it was reused seven times. Cao *et al.* (2017) have recently compared the Ru/ZrO<sub>2</sub>@C SAC with the traditional Ru/C catalyst for hydrogenation of biomass-derived levulinic acid to  $\gamma$ -valerolactone. Although the Ru/C had good activity and selectivity in the 1<sup>st</sup> run, its activity dropped rapidly after the 3<sup>rd</sup> run, which led to the conversion rate of levulinic acid decreasing from 69.2% to 40%. At the same reaction conditions, the activity and selectivity of Ru/ZrO<sub>2</sub>@C remained almost unchanged after the 6<sup>th</sup> run. All these examples have shown that single atom catalysis has great potential in improvement of lignocellulosic conversion.

As discussed above, some progress has been made in using the single atom catalysis to improve lignocellulosic conversion. However, single atom catalysis is still being developed and tested; technical issues will need to be addressed before it is in practical use. More efforts should be made in such aspects as fully understanding the strong interactions between the active metal atoms and the supports involved in the SACs and how these interactions affect their catalytic performances; the controllable and facile preparation of SACs with finely and densely dispersed single atoms; and the robust stabilization of the highly dispersed single atoms under actual reaction conditions. After the joint efforts of different research teams, it is reasonable to expect that the single catalysis will put into practical use in chemical conversion of lignocellulosic biomass in the near future.

### Acknowledgments

This work was supported by the Graduate Innovative Fund of Wuhan Institute of Technology CX2017135.

### References Cited

- Cao, W., Luo, W., Ge, H., Su, Y., Wang, A., and Zhang, T. (2017). "UiO-66 derived Ru/ZrO<sub>2</sub>@C as a highly stable catalyst for hydrogenation of levulinic acid to  $\gamma$ -valerolactone," *Green Chem.* 19(9), 2201-2211. DOI: 10.1039/C7GC00512A
- Chen, F., Xie, S., Huang, X., and Qiu, X. (2017). "Ionothermal synthesis of Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles as efficient heterogeneous Fenton-like catalysts for degradation of organic pollutants with H<sub>2</sub>O<sub>2</sub>," *J. Hazard. Mater.* 322, 152-162. DOI: 10.1016/j.jhazmat.2016.02.073
- Chen, R., Zhu, S., Chen, C., Cheng, B., Chen, J., and Wu, Y. (2014). "Reviving the acid hydrolysis process of lignocellulosic material in biorefinery," *BioResources* 9(2), 1824-1827. DOI: 10.15376/biores.9.2.1824-1827
- Ding, Y., Zhu, S., Yu, P., Cheng, S., and Wu, Y. (2012). "Can lignocellulosic hydrocarbon liquids rival lignocellulose-derived ethanol as a future transport fuel," *BioResources* 7(4), 4493-4494. DOI: 10.15376/biores.7.4.4493-4494
- Du, Z., Chen, F., Lin, Z., Li, X., Yuan, H., and Wu, Y. (2015). "Effect of MgO on the catalytic performance of MgTiO<sub>3</sub> in urea alcoholysis to propylene carbonate," *Chem. Eng. J.* 278, 79-84. DOI: 10.1016/j.cej.2014.12.033
- Kyriakou, G., Boucher, M., Jewell, A., Lewis, E., Lawton, T., Baber, A., Tierney, H., Flytzani-Stephanopoulos, M., and Sykes, E. (2012). "Isolated metal atom geometries

- as a strategy for selective heterogeneous hydrogenations,” *Science* 335, 1209-1212. DOI: 10.1126/science.1215864
- Liu, G., Robertson, A., Li, M., Kuo, W., Darby, M., Muhieddine, M., Lin, Y., Suenaga, K., Stamatakis, M., Warner, J., and Tsang, S. (2017). “MoS<sub>2</sub> monolayer catalyst doped with isolated Co atoms for the hydrodeoxygenation reaction,” *Nature Chem.* 9(8), 810-816. DOI: 10.1038/nchem.2740
- Liu, W., Chen, Y., Qi, H., Zhang, L., Yan, W., Liu, X., Yang, X., Miao, S., Wang, W., Liu, C., Wang, A., Li, J., and Zhang, T. (2018). “A durable nickel single-atom catalyst for hydrogenation reactions and cellulose valorization under harsh conditions,” *Angewandte Chemie International Edition* 57(24), 7071-7075. DOI: 10.1002/anie.201802231
- Qin, Y., Xiong, Z., Ma, J., Yang, L., Wu, Z., Feng, W., Wang, T., Wang, W., and Wang, C. (2017). “Enhanced electrocatalytic activity and stability of Pd nanoparticles supported on TiO<sub>2</sub>-modified nitrogen-doped carbon for ethanol oxidation in alkaline media,” *Int. J. Hydrog. Energ.* 42(2), 1103-1112. DOI: 10.1016/j.ijhydene.2016.09.060
- Wang, T., Meng, Y., Qin, Y., Feng, W., and Wang, C. (2018). “Removal of furfural and HMF from monosaccharides by nanofiltration and reverse osmosis membranes,” *J. Energ. Inst.* 91(3), 473-480. DOI: 10.1016/j.joei.2017.01.005
- Yang, C., Li, R., Cui, C., Wu, J., Ding, Y., Wu, Y., and Zhang, B. (2017). “The pyrolysis of duckweed over a solid base catalyst: Py-GC/MS and TGA analysis,” *Energy Sources Part A-Recovery Util. Environ. Eff.* 39(2), 177-183. DOI: 10.1080/15567036.2016.1214641
- Zhang, L., He, Y., Yang, X., Yuan, H., Du, Z., and Wu, Y. (2015). “Oxidative carbonylation of phenol to diphenyl carbonate by Pd/MO–MnFe<sub>2</sub>O<sub>4</sub> magnetic catalyst,” *Chem. Eng. J.* 278, 129-133. DOI: 10.1016/j.cej.2014.11.096
- Zhu, S., Huang, W., Huang, W., Wang, K., Chen, Q., and Wu, Y. (2015a). “Coproduction of xylose, lignosulfonate and ethanol from wheat straw,” *Bioresour. Technol.* 185, 234-239. DOI: 10.1016/j.biortech.2015.02.115
- Zhu, S., Huang, W., Huang, W., Wang, K., Chen, Q., and Wu, Y. (2015b). “Pretreatment of rice straw for ethanol production by a two-step process using dilute sulfuric acid and sulfomethylation reagent,” *Appl. Energ.* 154, 190-196. DOI: 10.1016/j.apenergy.2015.05.008
- Zhu, S., Wang, K., Huang, W., Huang, W., Cheng, B., Chen, J., Zhang, R., Chen, Q., and Wu, Y. (2016). “Acid catalyzed hydrolysis of lignocellulosic biomass in ionic liquids for ethanol production: Opportunities & challenges,” *Bioresources* 11(1): 3-5. DOI: 10.15376/biores.11.1.3-5
- Zhu, S., Luo, F., Huang, W., Huang, W., Wu, Y. (2017). “Comparison of three fermentation strategies for alleviating the negative effect of the ionic liquid 1-ethyl-3-methylimidazolium acetate on lignocellulosic ethanol production,” *Appl. Energ.* 197, 124-131. DOI: 10.1016/j.apenergy.2017.04.011
- Zhu, S., Yang, M., Luo, F., Yang, X., and Xue, Y. (2018). “Engineering cell wall-degrading enzymes into growing plants to improve lignocellulosic ethanol production,” *BioResources* 13(1), 3-5. DOI: 10.15376/biores.13.1.3-5