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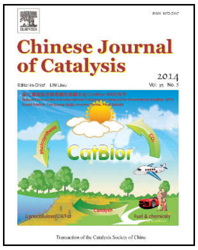

Review (Special Issue on the 2nd International Congress on Catalysis for Biorefineries (CatBior 2013))

One-pot catalytic conversion of cellulose to ethylene glycol and other chemicals: From fundamental discovery to potential commercialization

Mingyuan Zheng, Jifeng Pang, Aiqin Wang, Tao Zhang *

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China

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ABSTRACT

The one-pot catalytic conversion of cellulose to ethylene glycol (CEG) is a highly attractive way for biomass utilization to lessen the consumption of fossil energy resources. In this paper, we reviewed the disclosure of the CEG process and the rapid progress in the development of highly efficient and robust catalysts for it. Based on our study of tungstenic catalysts, we discuss the reaction mechanism, in which the reaction routes, catalyst states, and catalytic roles of the tungsten species and hydrogenation sites in the cascade reactions are understood clearly. With future applications in mind, the conversion of raw cellulosic biomass and the strategy to develop an efficient CEG process for commercialization are discussed, and a model where the CEG process is incorporated into a bio-refinery process of acetone-*n*-butanol-ethanol (ABE) production is presented.

1. Introduction

The growth of the world economy is currently heavily dependent on fossil energy, which has led to grave resource depletion and global environment deterioration. Faced with the great challenges of sustainable development, people are starting to turn towards a variety of clean and renewable energy resources, including hydraulic energy, wind energy, solar energy, and biomass energy to explore new technologies for improving the present situation [1–4].

Cellulose, a nature polymer of carbohydrates, is the most abundant biomass with a huge global production of up to 70 billion ton/year [5]. It stores solar energy and is composed of C, H, and O atoms, which are the fundamental elements of daily chemicals. Furthermore, cellulose is inedible and exists widely in the residues of agriculture and forestry. Therefore, its utilization will not impose a negative effect on food supply nor occupy farming lands. In the past decade, a vast effort has been devoted to the catalytic conversion of cellulosic biomass to fuels and chemicals, which formed a research revival after the first study peak in the 1980s [6–30]. As summarized in many comprehensive reviews, the conversions involve the production of 5-hydroxymethyfurfural and its derivates [16], levulinic acid [25], gamma-valerolactone [26,30], polyols [18,21,23,24], lactic acid [12,28,29], phenols [13,22], etc.

Ethylene glycol (EG) is the largest bulk polyol with a global consumption of up to 21 million ton/year. It is widely used in the synthesis of polyester, antifreeze, etc., and is estimated to have an increasing demand in the coming decades [31]. Currently, EG is mainly produced from petroleum ethylene by selective catalytic oxidation and hydration processes. Some recent endeavors have also been made for the catalytic prepara-

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* Corresponding author. Tel: +86-411-84379015; Fax: +86-411-84691570; E-mail: taozhang@dicp.ac.cn

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tion of EG from coal, which is also a fossil carbon resource [32,33]. Using cellulose to synthesize EG would notably contribute to alleviating the dependence on fossil energy resources and cut down on CO_2 emission. Meanwhile, this process could keep all the atoms from cellulose in the products, and thus it would have a very high atom economy, which is required for green chemistry.

Cellulose is composed of glucan units, which are connected in chains by β-1,4-glucosidic bonds and form crystalline three dimensional network by inter- and intra-molecular hydrogen bonds. The robust structure of cellulose makes it inert in most solvents and resistant to degradation. The challenges in the catalytic conversion of cellulose to chemicals have three aspects as follows. i) The process should be environmentally benign. The conventional conversion of cellulose by hydrolysis with inorganic acids needs to be replaced by novel green techniques. ii) There is a conflict between the harsh reaction conditions and high reaction selectivity, which needs to be balanced. The stability of cellulose requires harsh reaction conditions for the conversion. However, this is disadvantageous for obtaining target products with high selectivity. iii) The process should be simple. A more complex process has more energy loss and less efficiency in the route of biomass conversion.

In 2006, Fukuoka and coworkers [34] disclosed the one-pot catalytic conversion of cellulose to hexitols. By coupling the hydrolysis of cellulose to glucose and hydrogenation of glucose to stable sorbitol, the process overcame the problem of metastable glucose and obtained a high yield even at relatively high reaction temperatures. After 24 h reaction at 190 °C and 5 MPa H_2, cellulose was largely degraded into hexitols with a yield of 31% under hydrothermal conditions. The Pt/Al_2O_3 catalyst can be readily recycled by filtration after the reaction and reused several times. Liu and coworkers [35] further remarkably promoted the efficiency of this process by employing in situ protonic acid in near-critical water. After 30 min reaction at 245 °C, the hexitol yield was improved to 39.3% with a Ru/C catalyst. The green solvent of water, the heterogeneous catalyst that is readily recycled, and the simple one-pot process are the highlights of the work, which provide inspiration for the catalytic conversion of cellulose to useful polyol chemicals. In the following years, many researchers have extensively investigated the cellulose conversion in one-pot by coupling hydrolysis and hydrogenation to hexitols [36–51]. The catalysts used include Ni/CNF [39], Ni_2P/AC [40], Pt/BP2000 [42], Ru/$Cs_3PW_{12}O_{40}$ [44], Ru/AC-SO_3H [45], 1%Rh-5%Ni/MC [46], Ni/ZSM-5 [50], and solid hydrogenation catalysts in combination with heteropoly acids [38], and give hexitol yield in the range of 31.0%–86.1%.

With the target of developing less expensive but more effective and selective catalysts for the one-pot catalytic conversion of cellulose, we commenced the study of tungsten carbide catalysts for the biomass conversion. Under reaction conditions similar to that of Liu et al. [35], to our surprise, we found that over the tungsten carbide catalyst, cellulose was dramatically degraded into EG, which is a C_2 small molecule instead of the common products of hexitols that were mainly obtained with noble metal catalysts in the previous works. The highest EG yield reached 61% on an optimized nickel modified tungsten carbide catalyst in a one-pot catalytic process [52–54]. Because EG is a petroleum-dependent bulk chemical with high value and vast market demand, our new process of the one-pot catalytic conversion of cellulose to EG (CEG) has received extensive attention from both academic and industrial communities [21,24].

After the first report in 2008, more progresses in the study of CEG have been achieved in our laboratory and some other groups in the world [55–66]. Briefly, more effective tungsten carbide catalysts have been obtained by using optimal preparation methods or better supports, which further improved EG yields up to 75% [55,67]. Besides the tungsten carbides, a series of new types of catalysts have been explored. On tungstenic bimetallic catalysts, not only was high EG yield obtained, but also the polyol distribution can be effectively tuned, and the main reaction pathways were disclosed for guiding catalyst design [56]. Composite catalysts of tungstenic acid in combination with a hydrogenation metal catalyst were employed in the CEG process, which integrated homogenous and heterogeneous catalysis in one pot and had very good stability in a long period operation [59,63]. With the aim of the practical application of the CEG process, typical raw cellulosic biomass has been employed as the feedstock in the reaction to investigate the effect of pretreatment on the performance of the whole biomass conversion [58,60,61]. All these progress in the past several years have built a good foundation for understanding and utilizing the CEG process and made it a promising green technique for the EG production, which is still dominated by the traditional petrochemical industry to date. In 2013, we reviewed the series of work performed in our group and summarized our fundamental understanding of the reaction mechanism [24].

To more clearly depict the evolving route of the CEG process from fundamental disclosure to future potential application, in this paper, we first reviewed catalyst development for the CEG, including tungstenic catalysts and other types of catalysts. This is followed by a discussion on reaction mechanism understanding for catalyst design and product control. Then, we discuss the progress in the catalytic conversion of raw lignocellulosic feedstock and the strategies to improve reaction efficiency for the purpose of CEG process industrialization. Finally, after giving a model where the CEG process is integrated into a bio-refinery industry for acetone-*n*-butanol-ethanol (ABE) production, we give conclusions and comments on the future development of the CEG process.

2. Catalyst development for CEG

Catalysts for the one-pot catalytic conversion of cellulose to EG and chemicals can be classified two categories: (I) tungstenic catalysts and (II) other transition metal based binary catalysts (Table 1). Category I includes tungsten carbides, tungsten phosphides, tungstenic bimetallic catalysts, and tungsten acid based binary catalysts. The common feature in the performance of tungstenic catalysts (category I) is their unique high selectivity to EG, usually approaching 60%–75% and much lower yields of other polyols such as 1,2-propylene glycol