



Insights into the effect of the catalytic functions on selective production of ethylene glycol from lignocellulosic biomass over carbon supported ruthenium and tungsten catalysts

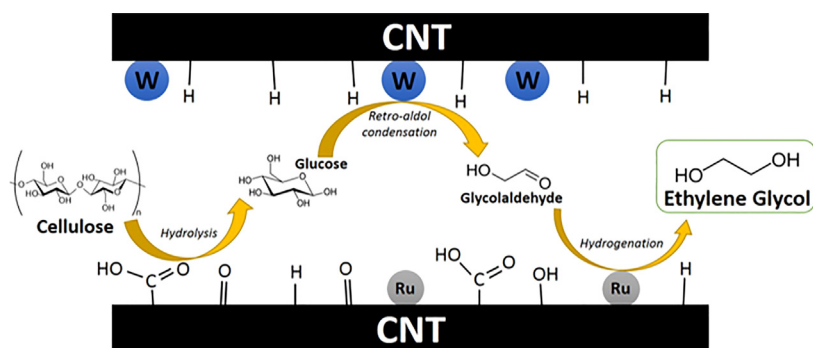


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GRAPHICAL ABSTRACT

A mixture of W and Ru catalysts supported on carbon nanotubes with oxygen-surface groups enhanced the production of ethylene glycol directly from cellulose, tissue paper and eucalyptus.



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ABSTRACT

The one-pot conversion of cellulose to ethylene glycol (EG) was investigated using a combination of a ruthenium catalyst supported on carbon nanotubes modified with nitric acid (Ru/CNT₁) and a tungsten catalyst supported on commercial non-treated carbon nanotubes (W/CNT₀). This physical mixture allowed to obtain an EG yield of 41% in just 5 h at 205 °C and 50 bar of H₂, which overcame the result obtained using a Ru-W bimetallic catalyst supported on commercial carbon nanotubes (35%) under the same conditions. Tissue paper, a potential waste cellulosic material, and eucalyptus were also tested under the same conditions and EG yields of 34 and 36%, respectively, were attained over the aforementioned catalytic physical mixture. To the best of our knowledge, this work presents for the first time the catalytic conversion of lignocellulosic materials, namely tissue paper and eucalyptus, directly into EG by an environmentally friendly process.

1. Introduction

Ethylene glycol (EG) is a valuable industrial chemical due to its important role in the synthesis of high-value chemicals that have a large

market demand, such as polymers (e.g. polyester fibers), antifreeze products and cosmetics (Cao et al., 2016; Zada et al., 2017; Zheng et al., 2017). However, EG is produced from petroleum-derived ethylene via multi steps of cracking, epoxidation and hydration. Recent endeavours

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have also been made for the production of EG from coal, which is also a fossil carbon resource (Zheng et al., 2014). Due to its importance, the production of EG by a sustainable process is vital to be achieved, which is the case of the one-pot hydrolytic hydrogenation of lignocellulosic biomass. Comparing to the petroleum-dependent multistep process, the lignocellulosic biomass path presents noticeable advantages of a renewable feedstock and one-pot process (Byun and Han, 2016; Deng et al., 2015; Kobayashi et al., 2014). However, the complexity of lignocellulosic biomass and its high resistance to chemical transformation make the production of chemicals directly from biomass still a challenge, which makes its investigation even more important. Lignocellulosic biomass is constituted of cellulose (35–50%), hemicelluloses (25–30%) and lignin (15–30%) (Deng et al., 2015; Kobayashi et al., 2012). As the greatest constituent of biomass, cellulose is the most promising natural resource for valuable chemicals production (Han and Lee, 2012; Yabushita et al., 2014). The process of cellulose transformation into EG can follow different reaction routes (Lazaridis et al., 2017; Tan et al., 2016; Zheng et al., 2017), where many types of reactions may occur (e.g. hydrolysis, *retro*-aldol condensation, hydrogenation, isomerization, dehydration, decarbonylation, dehydrogenation, hydration) and about 20 compounds can be produced as by-products or intermediates (Zheng et al., 2017). Firstly, cellulose is hydrolysed to glucose, which can be directly hydrogenated to hexitols or break its C–C bond to glycolaldehyde (GA) that is subsequently hydrogenated to EG. In the presence of bases (e.g. $\text{Ca}(\text{OH})_2$), glucose isomerizes into fructose, which then undergoes degradation to originate glyceraldehyde and/or dihydroxyacetone. These intermediates will then undergo dehydration and hydrogenation to form acetol, which is the precursor to 1,2-propylene glycol (PG) (Zheng et al., 2017). Therefore, the production of hexitols, EG and PG greatly depends on the competitive reactions including hydrogenation, C–C bond cleavage and isomerization, catalysed by hydrogenation sites (e.g. Ru), tungsten species and bases, respectively. Accordingly, the major reaction pathway for EG production comprises the following steps: hydrolysis of cellulose to oligosaccharides and glucose, usually catalysed by protons in situ generated reversibly from hot water or by additional acid; *retro*-aldol condensation (RAC) of glucose to glycolaldehyde (GA), catalysed by tungstic compounds; and hydrogenation of GA to EG, usually catalysed by Ru or Ni supported catalysts (Cao et al., 2016; Wang and Zhang, 2013).

The production of EG from biomass started in 1933 or earlier (Nemours, 1933), and for many decades the yield of the target diol was lower than 40%. Ji et al. reported for the first time an effective cellulose conversion to EG over a W_2C promoted nickel catalyst, achieving up to 61% EG yield after 30 min at 245 °C and 60 bar of H_2 (Ji et al., 2008, 2009). Since then, the yields of EG have been enhanced to 76% with bimetallic catalysts (Li et al., 2012; Zhang et al., 2010; Zheng et al., 2010) and the catalytic stabilities have been greatly improved using binary catalysts (Tai et al., 2013). The highest EG yield was achieved with Ni-W/SBA-15, but the catalyst could not be reused due to the complete collapse of the SBA-15 mesoporous structure (Zheng et al., 2010). Accordingly, the use of carbon as support is preferred due to its high resistance to acid and base attack and great stability under hydrothermal conditions (Wang and Zhang, 2013). It was also shown that not only W_2C , but also W, WO_3 or H_2WO_4 combined with Ni or noble metals (Ru, Pt, Pd) were effective for EG production (Li et al., 2017; Liu et al., 2012; Zheng et al., 2010). WO_3 was the most prone to becoming the main component of tungsten species, but there are still some unclear points on how it promotes the transformation (Li et al., 2017). Catalysts with tungstic compound are excellent choices to obtain EG, since tungsten species are highly active in promoting the selective C–C bond cleavage of glucose (Cao et al., 2014; Tai et al., 2013). Meanwhile, based on understanding of the reaction mechanism, the products

distribution could also be tuned (Liu et al., 2012; Liu and Liu, 2016; Zheng et al., 2010).

It was shown in our previous work (Ribeiro et al., 2018) that the catalyst containing Ru and W supported on commercial multi-walled carbon nanotubes was more catalytically effective for the one-pot direct cellulose conversion to EG than the physical mixture of the corresponding Ru and W monometallic catalysts. In continuation of that work, the surface chemistry of the carbon nanotubes was modified with nitric acid and its effect was investigated, showing that the EG yield was influenced by the presence of acid groups on the surface of the support. The catalytic reaction pathway for cellulose conversion to EG was proposed. Finally, the catalytic performance was evaluated for the conversion of tissue paper and eucalyptus to EG in aqueous solution, which, to the best of our knowledge, has not been reported anywhere yet. Many advances were made for catalytic conversion of pure cellulose, but the conversion of raw lignocellulosic biomass is still challenging and, herein, an efficient catalytic system is proposed.

2. Materials and methods

2.1. Preparation of materials

Microcrystalline cellulose (from Alfa Aesar), tissue paper (Renova) and eucalyptus (*Eucalyptus Globulus* from Portucel) were ball-milled in a Retsch laboratory equipment (Mixer Mill MM200) during for 4 h at 20 vibrations/s.

Commercial multi-walled carbon nanotubes (Nanocyl-3100, carbon purity > 95) were submitted to oxidative treatment with nitric acid ($\geq 65\%$, from Sigma-Aldrich) in order to obtain a material with a different surface chemistry. Accordingly, the commercial carbon nanotubes (CNT_0) were oxidized in a Pyrex round-bottom flask containing a 6 mol L^{-1} HNO_3 solution, and connected to a condenser. The acid solution was heated to boiling temperature, and the reflux stopped after 3 h. Subsequently, the oxidized material was washed with distilled water until neutral pH, and then dried overnight at 110 °C. The modified material was denoted as CNT_1 .

Tungsten and ruthenium monometallic catalysts were prepared by conventional incipient impregnation of commercial carbon nanotubes (CNT_0) with a solution of the corresponding metallic precursor. The metal precursors ruthenium (III) chloride (RuCl_3 99.9%, Ru 38% min.) and ammonium (meta)tungstate hydrate ($\text{H}_2\text{N}_6\text{O}_4\text{W}_{12}\cdot\text{aq}$ 99.999%, $\geq 85\% \text{ WO}_3$) were purchased from Alfa Aesar and Fluka, respectively. Briefly, the Ru catalyst was prepared by impregnation of CNT_0 with an aqueous solution of RuCl_3 . The support (CNT_0) was firstly introduced into an ultrasonic bath for 30 min and then the precursor solution was added dropwise, with a peristaltic pump (50 mL h^{-1}), until all the support was wet. Still in the ultrasonic bath, drying occurred for 90 min. After impregnation, the resulting catalyst was dried overnight at 110 °C and then submitted to thermal treatment under nitrogen flow ($50 \text{ cm}^3 \text{ min}^{-1}$ for 3 h) followed by reduction under hydrogen flow ($50 \text{ cm}^3 \text{ min}^{-1}$ for 3 h). Using the same procedure, the W catalyst was prepared by impregnation of CNT_0 with an aqueous solution of $\text{H}_2\text{N}_6\text{O}_4\text{W}_{12}$. The appropriate reduction temperatures (250 °C for Ru catalyst and 700 °C for W catalyst) were determined by temperature programmed reduction (TPR), and the thermal treatment was carried out at the same temperature. The samples were denoted as Ru/CNT_0 and W/CNT_0 . Following the same procedure, another Ru monometallic catalyst was prepared by impregnation of the modified support (CNT_1) and the resulting catalyst was denoted as Ru/CNT_1 . Furthermore, a Ru-W bimetallic catalyst was prepared by the impregnation of an aqueous solution of RuCl_3 on the already prepared W/CNT_0 catalyst (treated and reduced at 700 °C). The material was then treated and reduced at 250 °C and denoted as Ru-W/CNT_0 . For all the above catalysts, nominal metal

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