



Catalytic conversion of cellulosic biomass to ethylene glycol: Effects of inorganic impurities in biomass



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HIGHLIGHTS

- Effects of 16 impurities on conversion of cellulose to EG were investigated.
- Some ions changed the solution pH and therefore decreased EG yields.
- Ca and Fe ions decreased EG yield by reacting with W ion to form insoluble compounds.
- The pH and the W ion concentration should be 5–6 and >187 ppm for high EG yields.
- After removal of lignin and most harmful ions, EG yields could reach 50%.

GRAPHICAL ABSTRACT

The effects of inorganic impurities in biomass on the catalytic conversion of cellulose to ethylene glycol (EG) were investigated, and the mechanisms of catalyst deactivation by certain impurities were identified. The impurities in biomass were selectively removed, using suitable pretreatments, and the EG yield reached 50%, even for conversion of an industrial cellulosic feedstock at a high concentration of 10%.



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ABSTRACT

The effects of typical inorganic impurities on the catalytic conversion of cellulose to ethylene glycol (EG) were investigated, and the mechanism of catalyst deactivation by certain impurities were clarified. It was found that most impurities did not affect the EG yield, but some non-neutral impurities or Ca and Fe ions greatly decreased the EG yield. Conditional experiments and catalyst characterization showed that some impurities changed the pH of the reaction solution and affected the cellulose hydrolysis rate; Ca and Fe cations reacted with tungstate ions and suppressed the retro-aldol condensation. To obtain a high EG yield, the pH of the reaction solution and the concentration of tungstate ions should be respectively adjusted to 5.0–6.0 and higher than 187 ppm. For raw biomass conversion, negative effects were eliminated by suitable pretreatments, and high EG yields comparable to those from pure cellulose were obtained.

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1. Introduction

Lignocellulosic biomass is one of the most promising feedstocks for clean production of chemicals and fuels, because it is carbon-neutral, non-edible, and abundant (Corma et al., 2007; Kobayashi and Fukuoka, 2013; Ruppert et al., 2012; Zhou et al., 2011).

Lignocellulosic biomass consists mainly of cellulose, lignin, and hemicellulose. Hemicellulose and cellulose are polysaccharides composed of pentoses and hexoses, and these account for 50–85 wt% of lignocellulosic biomass. Differently, lignin is a phenolic polymer with a three-dimensional structure, and is covalently linked to hemicellulose and cellulose (Hu and Ragauskas, 2012; Kobayashi et al., 2012). In the plant cells of lignocellulosic biomass, the three components are connected with each other, forming rigid structures, which are recalcitrant to degradation under biological

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or chemical conditions. The one-pot conversion of lignocellulosic biomass to chemicals or fuels with high selectivity and efficiency is still a challenge (DeMartini et al., 2013; Himmel et al., 2007). Generally, it is necessary to separate the three components and then convert them individually (Hendriks and Zeeman, 2009; Mosier et al., 2005; Zhu and Zhuang, 2012).

In recent decades, various methods and techniques have been explored for the catalytic conversion of polysaccharides and lignin to chemicals and fuels (Alonso et al., 2012; Fukuoka and Dhepe, 2006; Gallezot, 2012; Ji et al., 2008; Luo et al., 2007; Zakzeski et al., 2010). Among these processes, the one-pot conversion of polysaccharides to ethylene glycol (EG) is very attractive for the large scale use of lignocellulosic biomass. First, this is a highly atom-economic process, because most of the C, H, and O atoms are retained in the final products. Second, EG is a valuable bulk chemical, and its global productivity reached 30 million metric tons in 2013, with an increase of 5–10% per year in past the five years (Yue et al., 2012). Finally, a series of highly efficient and robust catalysts have been developed for this process (Wang and Zhang, 2013; Zheng et al., 2014). Since the first report of tungsten carbide catalysts giving 61% EG yields in cellulose conversion (Ji et al., 2008, 2009), the EG yields have been improved to 76% with bimetallic catalysts (Zhang et al., 2010; Zheng et al., 2010) and the catalyst stabilities have been greatly enhanced by using binary catalysts (Tai et al., 2013, 2012). Meanwhile, the products distribution can be tuned based on the understanding of the reaction mechanism (Liu et al., 2012; Zheng et al., 2010).

Although great advances have been made for catalytic conversion of biomass to EG, particularly with pure cellulose as the feedstock, there are still some challenges in the conversion of raw lignocellulosic biomass. We previously reported that lignin and epidermal tissues inhibit the conversion of polysaccharides to EG. Pretreating the feedstock with an alkali and/or oxidant can effectively remove organic impurities and improve the EG yields (Li et al., 2012; Pang et al., 2014, 2011; Zhou et al., 2013, 2012). However, inorganic impurities incorporated in the biomass skeleton, such as Si, Ca, Na, cannot be completely removed by most pretreatment methods. Furthermore, the pretreatment process itself can also introduce inorganic species into the biomass, such as Na and Ca ions (Fahmi et al., 2007). The roles of such impurities in the pyrolysis or enzymatic conversion of biomass have been extensively studied (Eom et al., 2012; Patwardhan et al., 2010; Vanassche and Clijsters, 1990). Nevertheless, the catalytic conversion of cellulose to EG is conducted under conditions quite different to those for pyrolysis and enzymatic conversion, and the effects of impurities have yet to be thoroughly investigated. Herein, we studied the effects of typical metal ions, metallic powders, and metal oxides on cellulose conversion, based on the analysis of the impurities contained in the biomass. The mechanisms of catalyst deactivation caused by certain impurities were identified, based on an investigation of pH and concentration of tungstate ions in the reaction solution. Furthermore, the study of the effects of impurities on pure cellulose conversion was extended to raw biomass, and different pretreatment methods were developed to minimize the negative effects of impurities. This work provides valuable guidance for the practical development of catalysts and pretreatment methods for the large scale conversion of biomass to glycols.

2. Methods

2.1. Materials

Microcrystalline cellulose of particle size 50–200 μm was purchased from the Merck chemical company. Chemicals including

NaCl, MgCl_2 , CaCl_2 , FeCl_2 , AlCl_3 , NaNO_3 , NaAlO_2 , Na_2SiO_3 , Na_2HPO_4 , SiO_2 , Al_2O_3 , Fe_2O_3 , metallic Al and Fe powders were purchased from the Tianjin Kemiou Chemical Reagent Co., Ltd. *Miscanthus* was obtained from Hunan Province, China. Before pretreatment, it was dried at 393 K overnight, milled, and screened into powders of particle size smaller than 60 meshes.

Tungstic acid was purchased from the Aladdin Chemistry Co., and Raney Ni (311) catalyst was provided by the GRACE Co.

2.2. Pretreatment methods

Before reaction, *Miscanthus* (<60 meshes) was pretreated with $\text{Ca}(\text{OH})_2$ or NaOH solution in a three-neck flask. Typically, 10 g of *Miscanthus* was charged into a three-neck flask with 150 ml of base solution (1 wt% for $\text{Ca}(\text{OH})_2$; 0.5 wt% for NaOH) and a condenser, then the mixture was heated to 333 K within 20 min, and maintained at that temperature for 12 h. Finally, the *Miscanthus* was filtered, washed with 5 L of water and dried at 393 K for 12 h.

An industrial feedstock of corn cob cellulose was received from Songyuan, Jilin Province, China. The hemicellulose and lignin in the corn cob were removed by acid and alkaline treatments. Before use as a feedstock, it was washed to neutral with deionized water and then dried at 393 K for 12 h.

2.3. Analytical methods

The compositions of the *Miscanthus* and corn cob cellulose were analyzed based on the Van Soest method. The inorganic elements in the raw and pretreated biomass were analyzed using X-ray fluorescence (XRF). Before analysis, the samples were diluted with boric acid.

X-ray diffraction (XRD) patterns of the solid residues after removal of Raney Ni by magnetic separation were collected on a PW3040/60 X' Pert PRO (PANalytical) diffractometer equipped with a $\text{Cu K}\alpha$ radiation source ($\lambda = 0.15432 \text{ nm}$), operating at 40 kV and 40 mA. A continuous mode was used for recording data at a scanning speed of $5^\circ/\text{min}$.

The pH of the solution before reaction was monitored using a pH meter (Eutech CyberScan pH 510) at 298 K. Before measurement, the mixture in autoclave including catalysts, feedstock, and water was stirred for 30 min.

The tungstate ions in the liquid phase after the reaction were determined by using inductively coupled plasma-atomic emission spectrometry (IRIS intrepid II XSP instrument, Thermo Electron Corporation).

2.4. Catalytic reaction

The catalytic conversion of cellulose was performed in a stainless-steel autoclave (Parr Instrument Company) lined with Hastelloy alloy. For control experiments, microcrystalline cellulose (1.0 g), catalyst (0.12 g Raney Ni and 0.12 g tungstic acid), impurity (0.075 g), and water (100 g) were charged in a 300 mL autoclave; the reaction was performed at 518 K for a designed reaction time, with a stirring speed of 800 rpm.

For lignocellulosic biomass conversion, feedstock (4.44 g), catalyst (0.53 g Raney Ni and 0.53 g tungstic acid), and water (40 g) were put in a 100 mL autoclave; the reaction was performed at 518 K for 3 h with a stirring speed of 800 rpm.

After reaction, the liquid phase products were filtered, and analyzed using a high-performance liquid chromatography (HPLC, Agilent 1200, Shodex Sugar SC1011 column, differential refractive index detector) system. The total organic carbon (TOC) in the liquid was determined using a TOC analyzer (LiquiTOC, elemental, Germany). The gas phase products were analyzed by using a gas chromatograph (Agilent 6890N) with a TDX-1 column.

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