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The use of organic waste-derived volatile fatty acids as raw materials of C_4-C_5 bioalcohols

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ABSTRACT

This study highlights a novel method for the production of bioalcohols, like 1-butanol, from organic waste-derived volatile fatty acids (VFAs) via non-biological pathways. A strategic two-step process was conducted to afford the bioalcohols. The process consists of esterification of VFAs to form VFA methyl esters (VFAMEs) followed by hydrogenation to bioalcohols. In the first step, carbon nanotubes was determined to be an effective carbon material to convert VFA to VFAME with high yields (>90%). In the second step, various metals (Pt, Pd, Rh, Ru, Ni, Co, and Cu) were tested and the inexpensive cobalt was the most active metal for hydrogenation of VFAMEs to their corresponding alcohols. The final yield of 1-butanol via the two-step process was 19 wt.%, which is comparable to that of conventional fermentation processes. Given the massive generation of organic waste, the two-step process to produce biobutanol has excellent potential for being developed in large scale.

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1. Introduction

Bioethanol is widely used to reduce the consumption of petro-based gasoline (Hashim et al., 2017). However, bioethanol has lower energy density and is more corrosive than conventional gasoline (Swana et al., 2011). To compensate for the shortcomings of bioethanol, the synthesis of $C_{4\text{-}5}$ bioalcohols (e.g., butanol and pentanol) is desirable because the inferior chemical properties of bioethanol are mainly due to its short carbon chain (Pfromm et al., 2010; Yusoff et al., 2015). In general, $C_{4\text{-}5}$ alcohols are less hydrophilic and less corrosive than bioethanol (Dürre, 2007; Kumar and Gayen, 2011). In addition, the physico-chemical properties of butanol more closely resemble those of gasoline, allowing it to act as an octane enhancer because of its low oxygen content (Wu et al., 2008). Thus, $C_{4\text{-}5}$ bioalcohols are better gasoline-blending agents than bioethanol (Alasfour, 1997; Yusoff et al., 2015) and the value of biobutanol based on demand projections is expected to reach approximately 18 billion USD by 2022 (GrandViewResearch, 2015). Nevertheless, commercialized platforms for producing biobutanol mainly rely on the fermentation of carbohydrates, so-called the acetone-butanol-ethanol (ABE) fermentation, because its major products are acetone, butanol, and ethanol (Jones and Woods, 1986). However, technology is lacking for the production of butanol via the fermentation (Mariano et al., 2012). For instance, an energy-intensive distillation process is inevitably required to produce moisture-free alcohol (Green, 2011). Due to intrinsic fermentation mechanisms which involve hydrolysis, the fermentation process also requires a large amount of water, which can reduce the economic viability of the procedure due to the requirement for post-treatment of wastewater (Green, 2011). The concentration of butanol produced from the fermentation process using genetically engineered *Clostridia* strains typically ranges from 4 to 19 g L^{-1} (Jang et al., 2012; Khedkar et al., 2017). This low concentration of butanol also contributes to the poor economics of the process because it necessitates a subsequent stringent concentration step (Bankar et al., 2013). Therefore, the development of novel non-biological process to produce renewable $C_{4\text{-}5}$ bioalcohols is urgently needed.

Significant efforts have been made to convert biodegradable waste (biowaste) into biogas via anaerobic digestion (AD) (Cavinato et al., 2017). Acidogenic products produced in the AD process (i.e., VFAs) can be strategically used as a chemical template for the

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production of bioalcohols. Biobutanol can be synthesized using butyric acid (generated from an acidogenic step in the AD process) via a two-step process: 1) esterification of the VFAs into VFA methyl esters (VFAMEs) and 2) hydrogenation of the VFAMEs into their corresponding alcohols. Given that conventional bioalcohol production (i.e., fermentation) relies on the conversion of a single component (e.g., carbohydrate), the strategic approach for synthesizing $C_{4\text{-}5}$ bioalcohols using VFAs represents a technical breakthrough in the fermentation of bioalcohols.

It was recently shown that carbon materials are effective for the first reaction (VFA esterification) (Lee et al., 2017). For the second step (ester hydrogenation), most studies have examined the hydrogenation of long-chain fatty acid alkyl esters (e.g., methyl palmitate and ethyl stearate) on metal catalysts such as Ru and Cu (He et al., 2013; Miyake et al., 2009). To the best of the authors' knowledge, studies regarding the hydrogenation of short-chain fatty acid methyl esters (VFAMEs) to synthesize alcohols have rarely reported (Pritchard et al., 2017). Thus, it is desirable to fundamentally study the hydrogenation of VFAMEs over different metal surfaces to produce their corresponding bioalcohols.

In this study, a strategic non-biological two-step process to produce $C_{4\text{-}5}$ bioalcohols from acidogenic products (VFAs) was investigated. To this end, a great emphasis was placed on the synthesis of VFAMEs from the acidogenic product VFAs (butyric acid, isobutyric acid, valeric acid, and isovaleric acid). VFAME synthesis was conducted non-catalytically at 1 bar using carbon nanotubes (CNTs). The synthesized VFAMEs were then converted into bioalcohols by hydrogenation over various metal catalysts such as Pt, Pd, Rh, Ru, Ni, Co, and Cu evaluate the efficacy of the catalytic systems. This study provides a novel pathway for the production of bioalcohols via a hybrid-process between chemical and AD processes. This study also demonstrates the use of VFAs as template chemicals for gasoline alternatives (i.e., bioalcohols).

2. Material and methods

2.1. Materials and catalyst preparation

Commercially available multi-walled CNTs (724769, Sigma-Aldrich), methanol (≥99.9%, Sigma-Aldrich), butyric acid (≥99%, Sigma-Aldrich), isobutyric acid (99%, Junsei Chemical), valeric acid (98%, Kanto Chemical), isovaleric acid (98%, Alfa Aesar), methyl butyrate (246093, Sigma-Aldrich), methyl isobutyrate (148008, Sigma-Aldrich), methyl valerate (148997, Sigma-Aldrich), and methyl isovalerate (36492, Sigma-Aldrich) were used as received.

Silica (SiO_2, specific surface area: 500 $m^2\,g^{-1}$, pore volume: 0.8 $cm^3\,g^{-1}$, pore size: 6 nm) purchased from Sigma-Aldrich (60741), was used as a catalyst support. Pt, Pd, Ru, and Rh (2 wt.%) as well as Ni, Co, and Cu (5 wt.%) catalysts were synthesized by incipient wetness impregnation with aqueous solutions of the following precursors: $Pt(NH_3)_4(NO_3)_2$ (278726, Sigma-Aldrich), $Pd(NH_3)_4(NO_3)_2$ (423823, Sigma-Aldrich), $Ru(NO)(NO_3)_3$ (373567, Sigma-Aldrich), $RhCl_3{\cdot}xH_2O$ (206261, Sigma-Aldrich), $Ni(NO_3)_2{\cdot}6H_2O$ (5608–4405, Dae-Jung Chemicals), $Co(NO_3)_2{\cdot}6H_2O$ (2571–4405, Dae-Jung Chemicals), and $Cu(NO_3)_2{\cdot}2.5H_2O$ (223395, Sigma-Aldrich). As an example of preparing the 5 wt.% Co/SiO_2 catalyst, 2.6 g of $Co(NO_3)_2{\cdot}6H_2O$ was dissolved in water. The solution was added drop wise to 10 g of the SiO_2 until incipient wetness. After incipient wetness impregnation, the metal salt solution-support mixture was dried at 90 °C for 12 h. The dried catalysts were then reduced at 300 °C (for Pt, Pd, Ru, Rh, Cu) or 550 °C (for Ni, Co) at a ramping rate of 5 °C min^{-1} under 20% H_2 in N_2 (50 mL min^{-1}) for 4 h.

2.2. Characterization

The specific surface area and pore volume of the CNTs were determined from N_2 adsorption-desorption isotherms at −196 °C using a Micromeritics ASAP 2020 instrument. To determine the diameter of the CNTs, Transmission electron microscopy (TEM) images were obtained using a Tecnai G2 T-20S microscope at 120 kV. A total of 50 diameters were measured to obtain the average diameter of the CNTs with a standard deviation.

Temperature-programed desorption (TPD) of the CNTs was performed to characterize its surface functionalities using a Micromeritics AutoChem 2920 instrument. For TPD analysis, a 100 mg CNT sample was loaded in a U-shaped quartz tube was heated 900 °C (5 °C min^{-1} ramp) with helium purge (25 mL min^{-1}). The amount of CO and CO_2 released from the sample during TPD was calibrated using the respective gases.

Uptake values for the metal surface sites were determined using different chemisorption methods. For Pt, Pd, Ru, Rh, Ni, and Co catalysts, static H_2 chemisorption was performed to determine their surface sites using a Micromeritics ASAP 2020 unit. Prior to H_2 chemisorption, the samples were reduced *in situ* under flowing H_2 at 300 °C for Pt, Pd, Ru, and Rh catalysts or at 550 °C for Ni and Co catalysts (1 °C min^{-1} ramp, 2 h), followed by helium purging for 2 h. After reduction and purging, the cell was evacuated for 2 h and cooled to 25 °C (for Pt, Ru, Rh, Ni, and Co catalysts) or 65 °C (for the Pd catalyst to avoid bulk Pd hydride formation (Joyal and Butt, 1987)). Hydrogen was dosed on the sample until and equilibrium pressure of 560 mmHg (1st isotherm). The amount of weakly adsorbed hydrogen was determined by evacuating the dosed hydrogen and subsequently repeating the hydrogen dosing (2nd isotherm). The amount of strongly adsorbed hydrogen was determined by subtracting the 2nd from the 1st isotherm. N_2O flow chemisorption was used to determine the number of Cu surface sites. The Cu catalyst sample was reduced *in situ* under flowing H_2 at 300 °C (1 °C min^{-1} ramp, 2 h). After reduction, the sample was cooled to 90 °C and the gas flow was switched to 2% N_2O in helium. The reaction of metallic Cu with N_2O produces N_2 gas and O on the surface of the catalyst. The surface stoichiometry of the O to Cu surface sites was determined to be 1:2, and the oxygen on the surface was quantified by monitoring N_2 evolution (N_2:O = 1:1) using a mass spectrometer (AT Frontier) with a Faraday cup and secondary electron multiplier.

2.3. Two-step process (esterification of VFA and hydrogenation of VFAME)

For the esterification of VFA (butyric acid, isobutyric acid, valeric acid, and isovaleric acid), VFA, MeOH, and CNTs were loaded in a batch reactor. The reactor was then sealed. Mixing the reactants and catalyst began at 700 rpm after the reactor was sealed. The reactor was heated to a target reaction temperature (20 °C min^{-1} ramp) and held at the target temperature for 10 s. After the reaction was complete, the reactor was chilled with 4 °C water. Each reaction was performed in triplicate to ensure reproducibility.

Batch reactions for the hydrogenation of VFAME (methyl butyrate, methyl isobutyrate, methyl valerate, and methyl isovalerate) were performed in a pressure vessel (100 mL) made by Ilshin Autoclave, equipped with a thermocouple to measure the actual reaction temperature. In a typical experiment, the reactor was loaded with 10 mL of methyl ester and 0.8 g of catalyst. Subsequently, the reactor was sealed, purged with hydrogen (ultra-high purity), and pressurized to the desired pressure. The pressurized reactor was heated using a band heater (10 °C min^{-1} ramp) and the desired reaction temperature was maintained. The reactant and catalyst in the reactor were stirred at 700 rpm and once the

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