Research article

Production of high-octane gasoline via hydrodeoxygenation of sorbitol over palladium-based bimetallic catalysts

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ABSTRACT

A methodology for the synthesis of gasoline-range fuels from carbon neutral resources is introduced. Sorbitol, a sugar-based compound, was employed as a raw material because the compound is readily obtained from cellulose. Gasoline-range hydrocarbons were produced via hydrodeoxygenation (HDO) on zirconium phosphate-supported Pd-bimetallic (Pt−Pd, Ru−Pd, Ni−Pd, Fe−Pd, Co−Pd, W−Pd) catalysts. Among the tested catalysts, the bimetallic W−Pd/ZrP catalyst exhibited the highest yield of gasoline products, peaking at ∼70%. However, with the bimetallic Fe−Pd and Co−Pd catalysts, high-octane gasoline products were made (research octane number (RON) of the products was higher than 100). The Fe−Pd catalyst also showed the highest initial activity for the HDO of sorbitol. This study demonstrates that HDO in the Pd-system is a promising option to produce high-quality gasoline-range hydrocarbons from lignocellulosic biomass.

1. Introduction

The heavy dependence of humans on petroleum resources, in conjunction with depleting fossil fuels, has triggered environmental problems, associated with energy security issues, that can be the driving force behind seeking new energy resources. Plant biomass (*e.g.*, lignocellulosic biomass) is one of these renewable sources with a high organic carbon content; fuels derived from renewable resources, such as biomass, may help to mitigate the current environmental issues. However, the lack of economical processes to convert lignocellulosic biomass into biofuels is one of the major impediments in harnessing biomass.

Lignocellulosic biomass can be decomposed into water-soluble carbohydrates (Moodley and Gueguim Kana, 2017; Zeng et al., 2013). The aqueous carbohydrates have been fermented into ethanol (*i.e.*, bioethanol) (Balat, 2011; Ben Yahmed et al., 2016), which could be used as a fuel. However, the fermentation of aqueous carbohydrates requires sterile conditions, a long residence time, and energy-intensive distillation of ethanol from water (Amin, 2009; Balat, 2011; Chng et al., 2017). To cope with these obstacles, hydrodeoxygenation (HDO) has been developed as a strategy for converting biomass-derived compounds (*e.g.*, sugars, sugar alcohols, and cellulose) into gasoline-range alkanes (Vilcocq et al., 2013; Zhao et al., 2011). Different reactions occur simultaneously or consecutively in HDO over a bi-functional catalyst that involves both metallic and acidic sites (Shabaker et al., 2003; West et al., 2009b). At the metallic sites, hydrogenation reactions and C–C bond cleavage by dehydrogenation/decarbonylation and dehydrogenation/retro-aldol condensation reactions occur. On the acidic sites, C–O bond cleavage via dehydration occurs. Isomerization occurs on the bi-functional sites between metals and acids (Kim et al., 2013; Li and Huber, 2010). However, HDO produces complex mixtures of chemical species in different phases. For instance, more than 50 chemical species were generated in both the gaseous and liquid phases after the HDO of sorbitol (Kirilin et al., 2010). Moreover, a computational reaction network model suggested that the reaction network for the HDO of sorbitol over a Pt/SiO$_2$–Al$_2$O$_3$ catalyst consists of ∼4800 reactions

and produces ~1180 chemical species (Moreno et al., 2013).

For HDO reactions, noble metals, such as Pt, supported on a solid acid support, have been widely used as bi-functional catalysts (Li and Huber, 2010; Vilcocq et al., 2014). The solid acid-supported catalysts are advantageous in terms of tuning the ratio of C–O to C–C bond cleavage by altering the ratio of metal to acid sites (Karanjkar et al., 2016; Lee et al., 2013). The atomic distance between the metallic and acidic sites is one of the crucial factors in determining the catalytic activity of the HDO reaction (Kim et al., 2013). Pt-based catalysts, supported on various solid acids such as SiO_2–Al_2O_3, metal oxides (*e.g.*, ZrO_2, Nb_2O_5, and TiO_2), and phosphates (Li et al., 2011b; Vispute and Huber, 2009; Xing et al., 2010), have been also studied for HDO reactions. Carbon-supported bimetallic Pt–Re was reported to produce monofunctionals via the HDO of sugar (*e.g.*, sorbitol, glucose) (Gurbuz et al., 2010; West et al., 2009a). It was also reported that Pt, supported on zirconium phosphate (Pt/ZrP), is more active for C–O cleavage but less active for the conversion of carbohydrates than carbon-supported Pt–Re (Pt–ReO$_x$/C) (Kim et al., 2013; Lee et al., 2017).

Other than Pt-based catalysts, Pd-based bimetallic catalysts are some of the most active metals for the hydrogenation of carbonyl groups, a critical fundamental reaction in the HDO of sugar alcohols (*e.g.*, xylitol, sorbitol) (Li and Huber, 2010; Moreno et al., 2013). Pd not only shows high alkane selectivity for the HDO of sorbitol (Huber et al., 2004) but also is ~50% cheaper than Pt (Mineral Commodity Summaries, 2017). Zirconium phosphate (ZrP) is a promising solid acid material for HDO reactions due to its high Brønsted/Lewis acid ratio and hydrothermal stability (Weingarten et al., 2011, 2013). However, there has been no systematic studies evaluating Pd-based bimetallic catalysts in HDO reactions. With respect to these findings, the aim of this study is to experimentally validate the feasibility to produce gasoline-range fuels with high octane numbers through the HDO of sorbitol over various Pd-based bimetallic catalysts supported on ZrP. Note that fuels with a high octane number are used in high-performance petrol engines. Sorbitol is considered a representative model compound for biomass-derived carbohydrates because it can be easily made via the hydrogenation of glucose (Gallezot et al., 1998). The results from this study could help design realistic hydrodeoxygenation processes to produce alternative gasoline from biomass-derived feedstocks.

2. Experimental

2.1. Catalyst preparation

The ZrP support was synthesized by the co-precipitation of ammonium phosphate monobasic ($NH_4H_2PO_4$; ≥98.5%, Sigma-Aldrich) and zirconium(IV) oxychloride octahydrate ($ZrCl_2O·8H_2O$; ≥99.5%, Sigma-Aldrich) (1 mol L^{-1} aqueous solutions, molar ratio of P to Zr = 2). The detailed procedure can be found in the literature by Okuhara and co-authors (Kamiya et al., 2004). The Pd was loaded onto the ZrP support by incipient wetness impregnation using a tetraamminepalladium(II) nitrate ($Pd(NH_3)_4(NO_3)_2$; 5.0 wt% as Pd, Strem Chemicals) aqueous solution. The Pd content in the catalyst was maintained at 3% by weight (denoted as 3 wt%). The impregnated sample was dried overnight at 90 °C, followed by calcination at 250 °C for 3 h in air. The Pd-based bimetallic catalysts were prepared by adding a metal salt solution, either tetraammineplatinum(II) nitrate ($Pt(NH_3)_4(NO_3)_2$; 99%, Strem Chemicals), ruthenium(III) nitrosyl nitrate ($Ru(NO)(NO_3)_3$; 1.5% Ru, Strem Chemicals), nickel(II) nitrate hexahydrate ($Ni(NO_3)_2·6H_2O$; ≥98.5%, Sigma-Aldrich), iron(III) nitrate nonahydrate ($Fe(NO_3)_3·9H_2O$; ≥98%, Sigma-Aldrich), cobalt(II) nitrate hexahydrate ($Co(NO_3)_2·6H_2O$; ≥98%, Sigma-Aldrich), or ammonium metatungstate hydrate (($NH_4)_6H_2W_{12}O_{40}·xH_2O$; 99.99%, Sigma-Aldrich), to the prepared 3 wt% Pd/ZrP catalyst using incipient wetness impregnation. The Pt−Pd and Ru−Pd molar ratios were fixed at 0.3. The Ni−Pd, Fe−Pd, Co−Pd, and W−Pd molar ratios were fixed at 3. The impregnated sample was dried overnight at 90 °C, followed by calcination at 250 °C for 3 h in air.

2.2. Catalyst characterization

Static H_2 chemisorption of the prepared catalysts was measured using an automated gas sorption analyzer (Autosorb iQ, Quantachrome Instruments). Prior to chemisorption analysis, a sample was reduced *in situ* at 300 °C (1 °C min^{-1} ramp, 2 h) in flowing H_2, followed by purging with helium for 2 h, evacuating for 2.5 h, and cooling to 30 °C. After the pre-treatment, the total amount of adsorbed hydrogen was measured by the amount of hydrogen dosed on the sample until it reached 560 mmHg equilibrium pressure. The cell was then evacuated, followed by the dosing of hydrogen on the sample to measure the amount of weakly adsorbed hydrogen. The amount of strongly adsorbed hydrogen was then determined by subtracting the amount of weakly adsorbed hydrogen from the total amount of adsorbed hydrogen. To determine surface area of the sample, N_2 physisorption was conducted at −196 °C using the automated gas sorption analyzer. Prior to the surface area analysis, the sample was degassed at 250 °C for 12 h.

2.3. HDO reaction

The HDO reaction was conducted using a high-pressure continuous flow reactor setup. A stainless-steel tube (Outer diameter: 6.35 mm; inner diameter: 5.46 mm; length: 30 cm) was used as a tubular reactor. The reaction temperature was controlled by a tube furnace (Thermcraft) connected to a PID controller. For the reaction, 3 g of a catalyst was loaded in the center of the reactor and both ends of the reactor were packed with glass wool. The catalyst was reduced *in situ* at 300 °C (1 °C min^{-1} ramp, 2 h) in flowing H_2 (100 mL min^{-1}) prior to the reaction. After the reduction, the reactor was cooled to the reaction temperature (245 °C) and then pressurized to 6 MPa by H_2. A back-pressure regulator was used to maintain the H_2 pressure during the reaction. An aqueous sorbitol solution (20 wt%) and H_2 gas (40 mL min^{-1}) were co-fed by an HPLC pump (Eldex Laboratories) and a mass flow controller (Brooks Instrument), respectively. The weight hourly space velocity (WHSV) was controlled by changing the feeding rate of the sorbitol solution. Liquid samples were taken periodically using a gas-liquid separator. The organic phase was extracted by using cyclohexane (99%, Acros Organics) to minimize the carbon loss from the vaporized organic species. Gaseous samples flowed through the back-pressure regulator (to maintain a system pressure of 6 MPa), and directly delivered to a gas chromatography (GC) system for analysis (see section 2.4 for details).

2.4. Product analysis

For the analysis of the gaseous samples produced from the HDO of sorbitol, an Agilent 7890A GC-flame-ionized detector (FID)/thermal conductivity detector (TCD) system (conditions: 35 °C for 5 min, 150 °C (5 °C min^{-1}) for 15 min; helium (2 mL min^{-1}) as the carrier gas) was connected to the reactor system to allow the direct injection of gaseous samples into the GC. Carbon monoxide (CO) and carbon dioxide (CO_2) were analyzed by a TCD equipped with an Agilent GS-Carbon PLOT column. Alkanes in the gaseous samples were analyzed by a FID equipped with a Restek Rt-Q-Bond column. For the analysis of the liquid samples (both aqueous and organic phases) produced from the HDO of sorbitol, an Agilent 7890A GC-FID equipped with a Restek Rtx-VMS column (conditions: 40 °C for 5 min, 240 °C (7.5 °C min^{-1}) for 15 min; helium (1.24 mL min^{-1}) as the carrier gas) and a Shimadzu LC-20AT HPLC with a UV–Vis and RI detector equipped with a Biorad Aminex HPX-87H column (conditions: 30 °C; 0.005 M H_2SO_4 (0.6 mL min^{-1}) as the mobile phase) were used. For all data points, mean values of replicates (n ≥ 3) are reported and standard deviations of the mean values of around 1%. Equations for calculating conversion, selectivity, yield, and WHSV are shown in supporting information.