



Gas-phase, catalytic hydrodeoxygenation of propanoic acid, over supported group VIII noble metals: Metal and support effects

Yuliana K. Lugo-José, John R. Monnier, Christopher T. Williams*

Department of Chemical Engineering, University of South Carolina, Columbia 29208, SC, USA

ARTICLE INFO

Article history:

Received 15 July 2013

Received in revised form 9 October 2013

Accepted 14 October 2013

Available online 19 October 2013

Keywords:

Biomass
Hydrodeoxygenation
Decarbonylation
Decarboxylation
Hydrogenation
Propanoic acid
Palladium catalyst

ABSTRACT

The catalytic, gas-phase hydrodeoxygenation (HDO) of propanoic acid (PAC) over supported group VIII noble metals (M = Pd, Pt, Rh, Ru, Ni) was studied at 1 atm and 200–400 °C. The activity and selectivity as a function of the reaction temperature was investigated. The reaction activity based on the TOF follows the order: Pd > Ru > Pt > Rh > Ni. The reaction over Pd, Pt and Rh catalysts proceeds mainly via decarbonylation (DCN) and decarboxylation (DCX) pathways at each reaction temperature. For Ru and Ni catalysts, while decarbonylation and decarboxylation pathways were predominant at lower temperatures (e.g., 200–250 °C), at higher temperatures (>300 °C) the formation of diethyl ketone was observed. Additionally, the kinetics of Pd over different supports (carbon, SiO₂ and TiO₂) were examined. The activity based on the TOF decreases in the following order: Pd/SiO₂ > Pd/TiO₂ > Pd/C. The reaction orders in acid and H₂ were found to be approximately 0.5 and zero, respectively, regardless of the support. The apparent activation energies studied in a temperature range of 200–240 °C, were 16.7 ± 0.6, 19.3 ± 1.6 and 11.7 ± 0.7 kcal/mole for Pd/C, Pd/TiO₂ and Pd/SiO₂ catalysts, respectively. The selectivity for Pd/C and Pd/SiO₂ indicated mainly decarbonylation/decarboxylation and hydrogenation reaction pathways. In contrast, Pd/TiO₂ at low temperatures (200 °C) could generate decarbonylation and esterification products.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The demand of energy is increasing constantly and the United States is dependent on foreign sources for about half of its fuel consumption [1]. The combustion of fossil fuels releases carbon dioxide, a major greenhouse gas, into the atmosphere contributing to the problem of global warming. This factor, along with the increasing demand for fossil fuels coupled with the decreasing availability of those resources, has prompted a move towards alternative energy production and utilization [2,3]. New research efforts promise to bring advances in a variety of areas, and biomass conversion to fuels and chemicals will play a critical role in the future.

Industrial processes for converting biomass into biofuels include gasification to syngas (leading to liquid fuels through FT synthesis), pyrolysis to produce bio-oil, and hydroprocessing to remove oxygen functionality [4–6]. During these processes, carbon dioxide is released as well; however, the emission gases are balanced largely by the carbon dioxide that is captured during the growth of the biomass, depending upon how much energy was used to grow, harvest and process the fuel [7]. Feedstocks derived from lignocellulosic substances contain great amounts of oxygen such that the

C:O ratio approaches unity. However, the fuel and chemical products derived from such feedstocks must have an oxygen content less than about 5.0% to be commercially viable [8,9]. Heterogeneous, catalytic deoxygenation (including hydrodeoxygenation) is one of the most promising processes for generating hydrocarbon fuels from biomass. During hydrodeoxygenation (HDO), hydrogen is co-fed with the reactant to facilitate hydrogenolysis (HYS) and hydrogenation reactions required for the removal of oxygen.

During the 1980s, Maier et al. studied the gas-phase decarboxylation of short chain carboxylic acids to hydrocarbons using Ni and Pd catalysts [10]. However, most of this work focused on C–C bond scission rather than removal or hydrogenation of the C=O bond. Since then, increasing amounts of research have been conducted in the area of biomass-derived platform molecules such as organic acids and esters (e.g., palmitic, oleic and stearic acid, ethyl stearate and tristearine) via decarboxylation and hydrogenation reactions on monometallic and bimetallic catalysts [11–28]. For example, Murzin and co-workers have focused on biomass-derived, liquid-phase hydrogenation on supported palladium catalysts [29], while Resasco and Lobban reported the direct conversion of triglycerides to olefins and paraffins over Pt/Al₂O₃, Pt/SiO₂, and PtSnK/SiO₂ catalysts [30]. Additionally, Kozhevnikov et al. recently reported studies on heteropoly acid and bifunctional metal-loaded heteropoly acid catalysts for the deoxygenation of PAC [31].

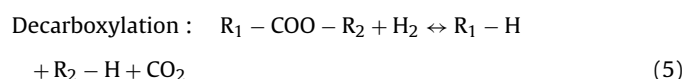
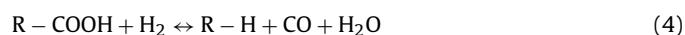
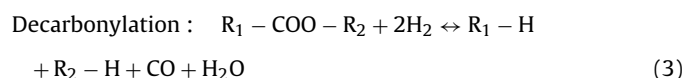
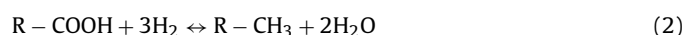
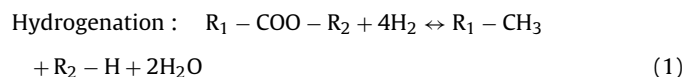
* Corresponding author. Tel.: +1 803 777 0143; fax: +1 803 777 8265.
E-mail address: willia84@cec.sc.edu (C.T. Williams).

Table 1
Physical and chemical properties of M/SiO₂.

Metal loading (wt%)	Catalyst Mx/SiO ₂	Calcination temp. (°C)	Reduction temp. (°C) 100% H ₂	Dispersion (%) O ₂ –H ₂ titr.	Particle diameter (nm)
1.1	Pd	300	350	3.9	31.4
4.0	Pd*	–	350	55.0	2.0
2.1	Pt	–	300	11.7	9.7
2.2	Rh	–	300	21.0	5.3
1.6	Ru	300	300	11.7	11.4
1.8	Ni	450	450	4.8	22.6

* Pd/SiO₂ synthesized by SEA.

Eqs. (1)–(6) illustrate the hydrogenation, decarbonylation, and decarboxylation pathways proposed for the HDO of organic acids and esters. In addition, the CO₂ and CO products from the decarboxylation (DCX) and decarbonylation (DCN) routes can undergo further reaction through water–gas shift and methanation, consuming large amount of H₂.



The present work aims to explore the catalytic chemistry of the HDO of PAC (a model compound for aliphatic organic acids) over supported group VIII noble metal catalysts. The monometallic catalysts have been selected based on their potential to catalyze different bond breaking events relevant to the above reactions. The catalysts include Pd, Pt, Ru, Rh and Ni supported on SiO₂. Additionally, Pd was screened on different supports (i.e. carbon, SiO₂, and TiO₂) to investigate the influence of the support material on activity, selectivity and activation energy. These studies provide insight on the different reaction pathways to form paraffins/olefins or oxygenated products from biomass derived organic acids.

2. Experimental

2.1. Catalyst synthesis (M/SiO₂)

For the screening reaction on M/SiO₂ (M = Pd, Ru, Ni), the catalysts were synthesized by incipient wetness utilizing aqueous solutions of the following metal salts: palladium nitrate hydrate (Pd(NO₃)₂·xH₂O, 99.9 Sigma-Aldrich), ruthenium nitrosyl nitrate (Ru(III)(NO)(NO₃)₃, 31.3% min Alfa Aesar) and nickel perchlorate hexahydrate (Ni(II)(ClO₄)₂·6H₂O, 99.99% Alfa Aesar). The SiO₂ support (Silica Star, S_{BET} = 100 m²/g) and the commercial catalysts of 2.14 wt% Pt and 2.06 wt% Rh over SiO₂, were obtained from BASF. In addition, a 4.0 wt% Pd catalyst with a different SiO₂ support (Aerosil 300, S_{BET} = 330 m²/g, Evonik) was synthesized by strong electrostatic adsorption (SEA), where the pH of the metal salt complex solution (200 ppm of [Pd(NH₃)₄]²⁺Cl₂, 99.9% Sigma Aldrich) was controlled based on the PZC of the SiO₂ [32,33]. Once the pH of the solution is acquired, the support was impregnated and shaken for 1 h. After the final pH was obtained, the difference (ΔpH) indicated that a strong electrostatic interaction between the metal

precursor and the –OH group on the support took place, allowing a controlled impregnation with highly dispersed metal precursors [34–36]. The catalysts prepared by SEA or incipient wetness were dried overnight at 70 °C, followed by calcination in air and reduction with 100% H₂ at their respective temperatures for 2 h (see Table 1). The exception was the 4 wt% Pd/SiO₂, which was not subjected to a calcination step due to the fact that the 1.1 wt% Pd/SiO₂ catalyst exhibited very large particle size. The commercial catalysts were already prepared, and therefore it was decided that no calcination step was required.

2.2. Catalyst synthesis (Pd/X)

Three different palladium catalysts were investigated for the detailed kinetics of the HDO of PAC: 4.0 wt% Pd/SiO₂ (Aerosil 300, S_{BET} = 330 m²/g, Evonik), 5.0 wt% Pd/C (CP-97, S_{BET} = 615 m²/g, commercial BASF catalyst) and 2.3 wt% Pd/TiO₂ (TiO₂, S_{BET} = 46.1 m²/g, Evonik). The Pd/SiO₂ and Pd/TiO₂ catalysts were synthesized by SEA, while the commercial Pd/C was supplied by BASF and followed the same procedure described in the previous section.

3. Pulsed H₂ chemisorption

The metal dispersions of the catalysts were determined by pulsed hydrogen titration of oxygen pre-covered sites using a Micromeritics 2920 AutoChem II Analyzer. Prior to the analysis, the catalysts (0.1–0.2 g) were reduced in flowing 100% H₂ for 2 h, followed by purging with Ar for 2 h to remove any physisorbed hydrogen. After cooling to 40 °C in flowing Ar, the catalysts were exposed to 10% O₂/He for 30 min followed by purging with Ar (30 min). Titration with pulses of 10% H₂/Ar was then employed until no further H₂ uptake occurred. This method was applied for Pd, Pt, and Rh based catalysts. For Ru and Ni, a modified hydrogen chemisorption method was implemented. The sample experienced the same pretreatment described previously; however, no H₂-chemisorption at 40 °C was done. After being exposed to argon, the sample was heated up to 100 °C by temperature programmed oxidation, following by flushing with argon for 30 min. Then, the sample temperature was raised up to 225 °C and exposed to 10% H₂/Ar. This titration temperature was confirmed based on the results of temperature programmed oxidation/reduction described in the Supplemental Information.

3.1. Catalyst evaluation

The activity and selectivity of each catalyst was measured for the HDO of PAC. The experiments were carried out in a single pass, packed bed, plug flow reactor system. The catalysts were reduced in-situ at temperatures ranging from 200 to 400 °C at a total flow of 50 sccm H₂ for 2 h at 1 atm pressure. The reduction temperature was chosen depending on the different reduction treatments required for each metal (Table 1). The feed stream for the screening experiments consisted of 1.0% PAC (Alfa Aesar, 99%) and 20% H₂,

Download English Version:

<https://daneshyari.com/en/article/40193>

Download Persian Version:

<https://daneshyari.com/article/40193>

[Daneshyari.com](https://daneshyari.com)