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Catalytic deoxygenation of octanoic acid over silica- and carbon-supported palladium: Support effects and reaction pathways

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ABSTRACT

Octanoic acid (OA) deoxygenation was investigated over silica- and carbon-supported palladium catalysts (each containing 5 wt.% Pd) at 235–300 °C and 1 atm in a continuous flow reactor. A commercial Pd/SiO₂ (A) catalyst was active for OA decarbonylation (DCN) and hydrodeoxygenation (HDO) at 260 °C under 10% H₂; subsequent hydrogenation (HY) and DCN of the primary products, 1-heptene and octanal, respectively, produced *n*-heptane. Under equivalent conditions, a Pd/SiO₂ (B) catalyst prepared using Pd(NO₃)₂ and Aerosil 300 produced *n*-heptane with very high selectivity (>99%) via DCN/HY. In contrast, a commercial Pd/C (A) catalyst was highly active and selective to *n*-heptane (>98%) and CO₂ (65%) under these conditions. Moreover, CO₂ selectivity and *n*-heptane yield increased with reaction temperature consistent with direct decarboxylation (DCX). Increasing H₂ partial pressure resulted in markedly lower activity and CO₂ selectivity; however, Pd/C (A) had negligible activity under He. Pd/C (A) exhibited greater water–gas shift (WGS) activity than Pd/SiO₂ (A); however, differences in WGS activity alone cannot explain the observed support effect. A more highly dispersed Pd/C (B) catalyst was more active at 260 °C under H₂ than Pd/C (A); however, under 10% H₂, it had lower activity, CO₂ selectivity (55%), and stability. Pd/C (A) and Pd/C (B) have very similar textural properties, but Pd/C (A) has a much higher Na content. By comparison, Pd supported on high-purity acetylene carbon black exhibited only DCN activity. These results indicate that carbon surface properties (e.g., polar functional groups, alkali metal content) influence the fatty acid deoxygenation performance of Pd/C catalysts.

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1. Introduction

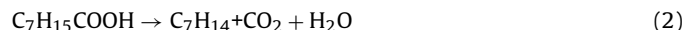
Environmental concerns continue to motivate research targeted at bio-renewable liquid transportation fuels (i.e., biofuels). Bioethanol and biodiesel are widely known substitutes for petroleum-derived gasoline and diesel, respectively; however, these oxygenated fuels eventually will be supplanted by hydrocarbon-based biofuels with higher energy densities, greater oxidative stabilities, and compatibility with existing engines and distribution infrastructure [1]. Saturated hydrocarbons for biofuels have been produced by catalytic deoxygenation of bio-derived triglycerides and fatty acids using supported palladium catalysts, specifically Pd/C [2–11]. The research reported herein focuses on gas-phase deoxygenation of octanoic acid (OA) over Pd/SiO₂ and Pd/C catalysts. Octanoate is the smallest saturated fatty acid ester found in the triglycerides comprising common biologically derived

fats and oils. Moreover, OA can be easily vaporized at temperatures of interest for fatty acid deoxygenation.

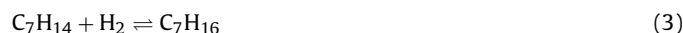
OA deoxygenation over Pd may occur via decarboxylation (DCX) and decarbonylation (DCN) pathways. Simple direct DCX produces *n*-heptane and CO₂:



Direct DCN produces 1-heptene, CO and H₂O:



Subsequent catalytic hydrogenation (HY) of 1-heptene produces *n*-heptane:



Eq. (2) can be combined with the water-gas shift (WGS) reaction:



and 1-heptene HY (Eq. (3)) to yield an indirect DCX pathway. The WGS reaction is reversible and exothermic with an equilibrium constant of 71.4 at 260 °C [12]; however, Pd supported on non-reducible metal oxides is known to have low WGS activity relative

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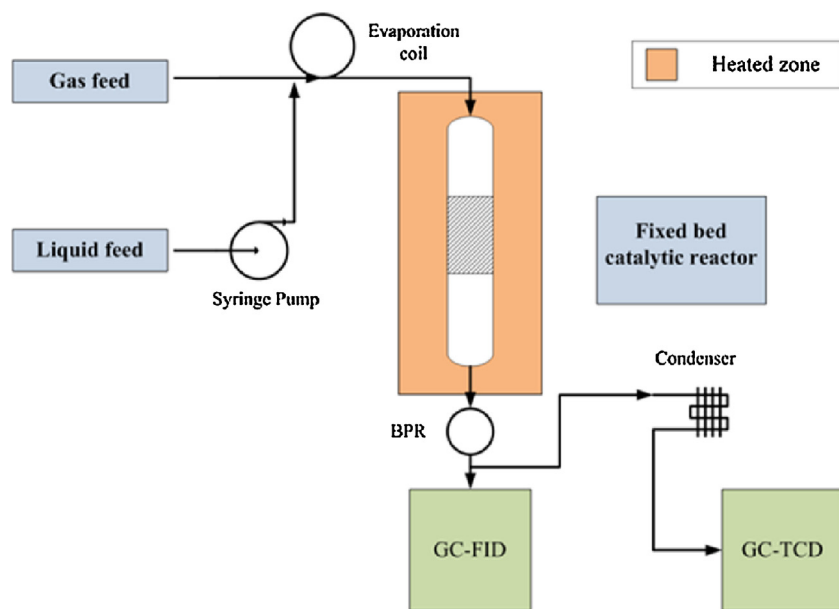


Fig. 1. Schematic diagram of fixed-bed catalytic micro-reactor with dual on-line gas chromatographs.

to other noble metals [13]. Early work by Maier, et al. [14] demonstrated that Pd/SiO₂ is an active and highly selective catalyst for gas-phase OA deoxygenation. OA was converted to *n*-heptane in 97% yield over Pd/SiO₂ at 330 °C and 1 atm in flowing H₂. More recently, Boda, et al. [15] investigated OA deoxygenation over Pd/C and concluded that in the presence of H₂ at elevated pressures, the reaction occurs via DCN. They proposed that OA DCN involves a formic acid intermediate that decomposes to CO and H₂O. Sun, et al. [16] reported that OA deoxygenation over Pd/SiO₂ at 260 °C and 1 atm also occurs primarily via DCN.

Computational chemistry methods have been employed to gain better understanding of the elementary steps involved in catalytic deoxygenation of fatty acids. Lu, et al., [17,18] investigated DCX and DCN of propanoic acid on Pd (1 1 1) using density functional theory. The more kinetically favorable DCN pathways involved α - and β -carbon dehydrogenation prior to C–C bond scission; the energy barrier for direct DCN was considered too high. The most kinetically favorable DCX pathway involved initial O–H scission followed by α -carbon dehydrogenation prior to C–COO cleavage. Overall, activation barriers for DCX were higher than for DCN. Lamb, et al. [19] used *ab initio* configuration interaction theory to investigate DCX of butanoic acid on the (1 1 1) surface of a Pd₄₂ nanoparticle. They concluded that adsorbed H influences reaction barriers and reference energies for surface intermediates by competing with O for Pd electrons. For example, with adsorbed H nearby, C₂H₅–CH–COO (ads) reacts to CO₂ and adsorbed propyl with a 32 kJ/mol barrier, whereas in the absence of adsorbed H, the barrier to form CO₂ and propylidene is 75 kJ/mol. However, the energy of the C₂H₅–CH–COO (ads) intermediate (relative to gas-phase butanoic acid) increases from 43 to 109 kJ/mol in the presence of adsorbed H, compensating for the lower decomposition barrier.

In this work, we systematically investigated gas-phase OA deoxygenation over Pd/SiO₂ and Pd/C catalysts in a continuous flow reactor. Commercial and lab-prepared catalysts containing 5 wt.% Pd were evaluated at 235–300 °C, and the effects of support, reaction temperature, and H₂ partial pressure on deoxygenation kinetics and reaction pathways were elucidated. In addition, representative Pd/SiO₂ and Pd/C catalysts were tested for WGS activity under reaction conditions similar to those employed for OA deoxygenation.

2. Experimental methods

2.1. Materials

OA (99%) was purchased from Fisher. Ultra-high-purity (99.99%) He, H₂ and 5% CO (balance He) were purchased from National Welders. Commercial 5 wt.% Pd/C catalysts (designated A and B, respectively) were purchased from Evonik–Degussa (E117) and Alfa Aesar (AA38300). A 5 wt.% Pd/SiO₂ catalyst (designated A, BASF Escat 1351), high-purity (99.99%) acetylene carbon black (200 mesh powder), and Pd(NO₃)₂·xH₂O were purchased from Strem Chemicals. A 5 wt.% Pd/SiO₂ (designated B) was prepared by incipient wetness impregnation of Aerosil 300 (Evonik–Degussa) with an aqueous solution of Pd(NO₃)₂. After drying at 100 °C in air, Pd/SiO₂ (B) was calcined at 400 °C in flowing zero-grade air (National Welders) for 2 h. A 5 wt.% Pd on carbon black catalyst [designated Pd/C (C)], was prepared by incipient wetness impregnation of acetylene carbon black with an aqueous solution of Pd(NO₃)₂. The resultant material was dried in air at 80 °C overnight and subsequently reduced *ex situ* at 400 °C in flowing H₂ for 1 h, cooled and purged with He, and passivated by slow air exposure.

2.2. Catalyst characterization

Specific surface area and pore volume were obtained by N₂ porosimetry using a Micromeritics ASAP 2020c instrument. The carbon-supported catalysts were degassed under vacuum at 300 °C for 8 h before N₂ physisorption measurements at 77 K. The Brunauer–Emmett–Teller (BET) and *t*-plot methods were used to determine the surface area and micropore volume, respectively. Pd dispersion was measured by CO pulse chemisorption using a custom-built apparatus [20]. Each sample was pretreated at 300 °C in flowing 5% H₂/Ar for 1 h then purged with He at same temperature for 30 min before cooling to 25 °C. Nominal Pd weight loadings and a CO/Pd surface atom stoichiometry of 0.6 [21] were used in dispersion calculations. Average Pd particle size (*d*, nm) was estimated from fractional dispersion (*D*) as $d = 1.12/D$ [22]. Transmission electron microscopy (TEM) of Pd/C (A) was performed at the NCSU Analytical Instrumentation Facility using a Hitachi HF2000 microscope. Catalyst samples were analyzed for Na and K at the NCSU

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