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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/SiO_2 (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

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http://dx.doi.org/10.1016/j.cattod.2015.12.021 0920-5861/© 2016 Elsevier B.V. All rights reserved. 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:

$$C_7H_{15}COOH \to C_7H_{16}+CO_2$$
 (1)

Direct DCN produces 1-heptene, CO and H₂O:

$$C_7H_{15}COOH \rightarrow C_7H_{14}+CO_2 + H_2O$$
 (2)

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

$$C_7H_{14} + H_2 \rightleftharpoons C_7H_{16} \tag{3}$$

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

$$\mathrm{CO} + \mathrm{H}_2\mathrm{O} \rightleftharpoons \mathrm{CO}_2 + \mathrm{H}_2 \tag{4}$$

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/SiO_2 is an active and highly selective catalyst for gas-phase OA deoxygenation. OA was converted to *n*-heptane in 97% yield over Pd/SiO_2 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/SiO_2 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 (111) 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 (111) 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 2h. A 5wt.% Pd on carbon black catalyst [designated Pd/C (C)], was prepared by incipient wetness impregnation of acetylene carbon black with an aqueous solution of $Pd(NO_3)_2$. 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% H_2/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

Environmental and Agricultural Testing Service using inductively coupled plasma-optical emission spectrometry (ICP-OES).

2.3. OA Deoxygenation experiments

Gas-phase catalytic deoxygenation of OA was investigated using an atmospheric pressure, fixed-bed micro-reactor equipped with dual on-line gas chromatographs. The apparatus is illustrated schematically in Fig. 1. The reactor consisted of a 0.5 in. OD stainless steel tube containing 0.5 g (typ.) catalyst powder suspended between quartz wool plugs. The reactor tube is mounted vertically in a single-zone tube furnace (Lindberg) with PID controller (Eurotherm). Catalyst temperature was measured using a Type K thermocouple in direct contact with the bed. Each catalyst was reduced in situ at 300 °C for 1 h in flowing H₂ (100 sccm). Gas flow rate and composition to the reactor were set by mass flow controllers, and liquid OA was fed by syringe pump (ISCO Series D) and evaporated prior to entering the reactor. Typical feed conditions were 4 µL/min OA injection rate and 100 sccm total gas flow rate. The total gas flow rate, H₂ partial pressure, reactor temperature, and OA injection rate were adjusted, as indicated, during the investigation. The reactor effluent was analyzed using an on-line gas chromatograph with flame ionization detector (GC-FID) for OA and organic reaction products and using an on-line GC with thermal conductivity detector (GC-TCD) for analysis of non-condensable gases (CO and CO₂). Alternatively, a quadrupole mass spectrometer (QMS) with an atmospheric-pressure gas inlet system was used for non-condensable gas analysis.

WGS reaction experiments were conducted in the same apparatus using 0.5 or 1.0 g catalyst powder suspended between quartz wool plugs. Under the standard test conditions, the feed gas contained 1.25% CO (25 sccm, 5% CO/He), and deionized (DI) water was injected resulting in a H₂O:CO molar ratio of unity. H₂ and He flow rates (75 sccm total) were adjusted to give a feed composition of 0, 10 or 75% H₂. The DI water injection rate was increased to achieve H₂O:CO ratios of 2 and 4.

2.4. Analytical methods

The GC-FID was a Shimadzu GC2010 equipped with an Econocap EC-1 capillary column. Periodic sampling was achieved using a Valco 6-port valve with a 100-µL sample loop. The GC column temperature was programmed as follows: 10 °C/min ramp from 70 °C to 100 °C, and then a 40 °C/min ramp to 240 °C. The FID responses were calibrated using a series of different concentrations of OA, *n*-heptane, 1-heptene, octanal and diheptyl ketone in suitable solvents. The GC-TCD was an SRI 8610C equipped with a Restek ShinCarbon ST 100 column operated isothermally at 100 °C. A standard calibration gas (5% CO, 5% CO₂, 5% H₂ and 1% CH₄) (National Welders) was used to calibrate the GC-TCD. The QMS system comprised a SRS RGA 100 instrument with a Pfeiffer capillary inlet system. The H₂ (2 m/z), He (4 m/z), CO (28 m/z), and CO_2 (48 m/z) ion currents were monitored routinely. The CO signal (28 m/z) was corrected for CO₂ electron fragmentation by subtracting 10% of the CO_2 (44 m/z) intensity. From GC and QMS data, the OA conversion, yields of *n*-heptane, 1-heptene and octanal, and CO₂ selectivity were determined.

3. Results

3.1. Catalyst characterization

 N_2 porosimetry, CO chemisorption, and Na ICP-OES results for the catalysts are given in Table 1. Pd/C (A) and Pd/C (B) have similar BET surface areas, total pore volumes, and micropore volumes. By comparison, the Pd/SiO₂ catalysts have lower surface areas, higher

100 nm 35 30 25 20 15 10 15 10 50

 $\label{eq:Fig.2.Bright-field\,TEM\,image(a) and particle-size\,histogram(b) of Pd/C(A) catalyst.$

8

Particle size (nm)

10

12

14

6

2

4

total pore volumes, and much lower micropore volumes. Pd/C (C) has the lowest BET surface area (by an order of magnitude relative to the activated carbon-supported catalysts) and total pore volume, and it has a negligible micropore volume, comparable to Pd/SiO_2 (B). Pd dispersions decrease in the order: Pd/C (B) > Pd/SiO₂ (B)>Pd/C (A)>Pd/C (C)>Pd/SiO₂ (A). The dispersions of Pd/SiO₂ (B), Pd/C (A), and Pd/C (C), however, are comparable indicating that these catalysts have similar Pd particle sizes. Pd particle sizes estimated from the dispersion data assuming a spherical particle morphology are included in Table 1. A TEM image and particle-size histogram of Pd/C (A) are shown in Fig. 2. The TEM average particle size is 7.1 nm in good agreement with the CO chemisorption result (6.9 nm). Pd/SiO₂ (A) and Pd/C (A) contain 0.5–1.0 wt.% Na, whereas Pd/C (B) contains only ~80 ppm Na. K concentrations were <50 ppm for these samples. Pd/SiO₂ (B) and Pd/C (C) was not analyzed for alkali metals, but the support materials used have high chemical purities, and alkali metals were not added during catalyst preparation.

3.2. OA deoxygenation over Pd/SiO_2

Temporal OA conversion and product yields over Pd/SiO_2 (A) at 260 °C under 10% H₂ are shown in Fig. 3a. OA conversion and *n*-heptane yield declined with time on stream (TOS), and 1-heptene and octanal yields increased concurrently. When the feed composition was switched to H₂ after 12 h TOS, OA conversion and *n*-heptane yield increased rapidly and approached 100%. Concomitantly, the effluent concentrations of 1-heptene and octanal

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Table 1 Summary of catalyst properties.

Catalyst	Pd dispersion ^a D (%)	Pd particle size d (nm) ^b	Surface area ^c (m ² /g)	Micropore volume ^d (cm ³ /g)	Total pore volume ^e (cm ³ /g)	Na conc. (wt.%)
Pd/SiO ₂ (A)	7.0	16.0	270	0.015	1.05	0.57
Pd/SiO ₂ (B)	19.7	5.7	220	0.002	1.19	-n/a-
Pd/C(A)	16.3	6.9	855	0.21	0.62	0.87
Pd/C(B)	42.0	2.7	810	0.17	0.68	0.0082
Pd/C(C)	14.8	7.5	80	0.006	0.29	-n/a-

^a Determined by pulse chemisorption using a CO:Pd surface atom stoichiometry of 0.6 [21].

^b Average spherical diameter estimated from Pd fractional dispersion (D) as d(nm) = 1.12/D [22].

^c BET surface area measured by N₂ adsorption at 77 K.

^d Determined using *t*-plot method.

^e Measured using N₂ at $p/p_0 = 0.97$ (77 K).



Fig. 3. (a) OA conversion and product yields with TOS over Pd/SiO₂ (A) at 260 °C and 1 atm (typ. feed conditions); (b) OA conversion and product yields over Pd/SiO₂ (A) at the indicated reaction temperatures, 1 atm (typ. feed conditions), and indicated H₂ mole percentages after 4 h TOS. Product selectivities indicated on bars.

decreased to negligible values; small concentrations of 1-octanol and *n*-octane were detected under these conditions. Only CO was detected by GC–TCD during OA deoxygenation indicating that DCN is the dominant reaction pathway. The CO yield closely matches the sum of *n*-heptane and 1-heptene yields throughout the experiment demonstrating that CO is produced in 1:1 stoichiometry to C_7 species.

The effects of temperature and hydrogen partial pressure on OA deoxygenation over Pd/SiO₂ (A) were further investigated using



Fig. 4. OA conversion, CO yield, and CO₂ yield with TOS over Pd/SiO₂ (B) at $260 \degree C$ and 1 atm (typ. OA feed conditions, H₂ mole percentage as indicated).

a fresh catalyst, and the results are shown in Fig. 3b. At 245 °C under H₂, OA conversion was ~70% and *n*-heptane selectivity was 95%; octanal was the only minor product observed. Changing the feed composition to 10% H₂ resulted in large decreases in conversion and *n*-heptane selectivity. Significant yields of octanal and 1-heptene were formed under these conditions. When the reaction temperature was increased to 260 °C, and subsequently to 300 °C, conversion and *n*-heptane selectivity increased incrementally. OA conversion and *n*-heptane selectivity approached 100% at 300 °C under 10% H₂.

Pd/SiO₂ (B) gave >80% initial OA conversion at 260 °C under 10% H₂ (Fig. 4). In contrast to Pd/SiO₂ (A), this catalyst did not deactivate rapidly with TOS. Moreover, *n*-heptane selectivity was >99% for the first 12 h TOS. Octanal and 1-heptene were not detected in significant yields over Pd/SiO₂ (B). Changing the feed composition to H₂ after 12 h, resulted in a modest increase in conversion (back to ~80%) with a slight (~1%) decrease in *n*-heptane selectivity. CO selectivity was high throughout the experiment: >91% initially under 10% H₂, increasing to ~98% after 12 h TOS, and >99% under H₂.

3.3. OA deoxygenation over Pd/C (A)

A fresh Pd/C (A) catalyst brought on stream at 260 °C under 10% H₂ exhibited >95% OA conversion with 65% CO₂ selectivity. Pd/C (A) maintained high activity and CO₂ selectivity under 10% H₂ over a period of 15 h TOS. The main organic product was *n*-heptane (>98%), although several minor products, including 1-heptene, octanal, 1- octanol, and *n*-octane, were detected under these conditions. When the catalyst temperature was decreased to 235 °C, OA conversion and CO₂ selectivity decreased to 38% and 40%, respectively. Concomitantly, octanal and 1-octanol yields *increased* at the expense of *n*-heptane, suggesting a lower activation energy for hydrodeoxygenation (HDO) than DCN/DCX. When the catalyst temperature

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Fig. 5. (a) OA conversion, *n*-heptane selectivity, and CO₂ selectivity; and (b) CO and CO₂ yields with TOS over Pd/C (A) at 260 °C and 1 atm (typ. OA feed conditions, H₂ mole percentage as indicated).

subsequently was increased to 260 °C, OA conversion and product selectivities returned to their previous levels (after accounting for catalyst deactivation).

When a fresh sample of Pd/C (A) was brought on stream at 260 °C under H₂, significantly lower initial OA conversion was observed (Fig. 5a). Only CO was produced (Fig. 5b), and the yields of CO and *n*-heptane were equivalent. Selectivity to *n*-heptane was ~92%, and HDO products (*n*-octane, 1-octanol, and octanal) were produced in significant yields. When the feed composition was switched to 10% H₂ after 6 h TOS, OA conversion, CO₂ selectivity, and *n*-heptane selectivity were due primarily to a large increase in CO₂ production (Fig. 5b). The catalyst deactivated slowly over the next 15 h TOS accompanied by decreasing CO₂ selectivity.

OA deoxygenation over Pd/C (A) was investigated at 300 °C using an 8 μ L/min injection rate resulting in a higher inlet OA concentration and weight hourly space velocity (WHSV). Initial OA conversion and CO₂ selectivity under H₂ were 80% and ~33%, respectively (Fig. 6a), and *n*-heptane selectivity was >98%. Octanal and 1-octanol were formed in very low yields, and *n*-octane was not detected under these conditions. After changing the feed composition to 10% H₂, complete OA conversion and ~75% CO₂ selectivity were observed. The higher CO₂ selectivity results from a large increase in CO₂ yield and a sharp decrease in CO yield (Fig. 6b).



Fig. 6. (a) OA conversion, *n*-heptane selectivity, and CO₂ selectivity; and (b) CO and CO₂ yields with TOS over Pd/C (A) at 300 °C and 1 atm (8 μ L/min OA injection rate, H₂ mole percentage as indicated).

Pd/C (A) deactivated more rapidly under 10% H₂ at 300 °C (with the higher OA feed concentration and higher WHSV) than at 260 °C. Concomitant with loss of activity, CO₂ selectivity dropped to 45% after 15 h TOS. The decline in OA conversion correlates with a decrease in CO₂ yield; CO yield actually increased slowly with TOS asymptotically approaching a steady state (Fig. 6b). During this period, 1-heptene yield increased resulting in a slow decline in *n*-heptane selectivity. Total CO + CO₂ yield is in excellent agreement with C₇ yield indicating closure of the material balance. When the feed composition was changed back to H₂ after ~17 h TOS, CO₂ yield decreased markedly (CO₂ selectivity <10%), but CO yield remained approximately constant.

Given the strong influence of H₂ partial pressure on conversion and product selectivity, OA deoxygenation over Pd/C (A) was tested using feed compositions ranging from 5 to 100% H₂ at 260 °C and 1 atm. OA conversion and CO₂ selectivity decrease with increasing H₂ partial pressure, as illustrated in Fig. 7. At lower H₂ partial pressures (5–10%), high OA conversions and CO₂ yields are observed suggesting that DCX of OA to *n*-heptane is the dominant reaction pathway. OA conversion and CO₂ selectivity decline markedly with increasing H₂ partial pressure primarily because of CO₂ yield loss. Concurrent with the decrease in CO₂ yield, CO yield increases slowly, and DCN becomes the dominant reaction pathway under H₂. C₇ yield and CO+CO₂ yield maintain a 1:1 relationship

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Fig. 7. OA conversion, *n*-heptane selectivity, and CO₂ selectivity over Pd/C (A) at various H₂ feed mole percentages at 260 °C and 1 atm (8 μ L/min OA injection rate). CO₂ selectivity for each H₂ feed composition calculated using the measured conversion and assuming WGS equilibrium.

throughout the range of H₂ partial pressures indicating formation of C₇ species via DCN and DCX. The *n*-heptane yield declines with increasing H₂ partial pressure because of HDO product formation. The dashed curve shown in Fig. 7 represents CO₂ selectivity as a function of H₂ partial pressure calculated using the experimental OA conversions and assuming WGS equilibrium [12]. Qualitative agreement with the experimental trend is observed; however, CO₂ selectivity under 5% H₂ is slightly greater and CO₂ selectivity under H₂ is much lower than predicted by WGS equilibrium.

Subsequently, Pd/C (A) was tested for OA deoxygenation activity at 260 °C under He using typical feed conditions. The yields of 1-heptene, *n*-heptane, and octanal with TOS are shown in Fig. 8a. Initially, the total yield of deoxygenation products was less than 10%, and hydrocarbon yields declined rapidly with TOS. Octanal yield was nearly zero initially and passed through a very weak maximum at \sim 2.5 h TOS. The CO and CO₂ mole fractions determined by on-line QMS during the same period are shown in Fig. 8b. During the first 4 h TOS, when the 1-heptene yield was greater than the *n*heptane yield, the CO mole fraction was also greater than the CO_2 mole fraction. These data suggest that direct DCN (Eq. (2)) is the dominant reaction pathway; however, *n*-heptane formation appears to correlate with CO_2 formation (*i.e.*, DCX). After ~10 h under He, the catalyst had deactivated almost completely. Sharp increases in *n*-heptane and CO yields were observed when the feed composition was changed to 10% H₂ after 13 h TOS; however, the deactivation incurred under He was essentially irreversible. Very small increases in octanal and 1-heptene yields also were observed. We infer that over the heavily deactivated Pd/C (A) catalyst, nheptane forms via direct DCN followed by HY.

3.4. OA deoxygenation over Pd/C (B)

OA deoxygenation over Pd/C (B) was investigated at $260 \,^{\circ}$ C under typical feed conditions. Initial OA conversion under H₂ was ~85% and CO₂ selectivity was 0% (Fig. 9a). In contrast to the behavior of Pd/C (A), changing the feed composition to 10% H₂ did not increase OA conversion; however, CO₂ selectivity did increase to ~55%. The higher CO₂ selectivity under 10% H₂ resulted from a decrease in CO yield and a nearly equal increase in CO₂ yield (Fig. 9b). During this period, the catalyst began to deactivate rapidly accompanied by decreasing CO₂ selectivity. The loss in activity with TOS was primarily due to decreasing CO₂ production. The catalyst appeared to stabilize after about 20 h TOS at 40% conversion and



Fig. 8. (a) Yields of *n*-heptane, 1-heptene and octanal; and (b) CO and CO₂ mole fractions with TOS over 5% Pd/C (A) under He at 260 °C and 1 atm (typ. OA feed conditions, H_2 mole percentage as indicated).

~32% CO₂ selectivity. When the feed composition was changed back to H₂, OA conversion actually decreased slightly; the loss of CO₂ yield was greater than the increase in CO yield. Yields of octanal, 1-octanol and *n*-octane increased significantly under H₂ resulting in 94% *n*-heptane selectivity compared with >97% under 10% H₂.

3.5. OA deoxygenation over Pd/C (C)

OA deoxygenation over Pd supported on carbon black [Pd/C (C)] was also investigated at 260 °C under typical feed conditions; results for fresh catalyst samples brought on stream under H₂ and 10% H₂ are shown in Fig. 10. Initial conversion was much higher under H₂ than under 10% H₂; however, the catalyst deactivated much more rapidly under H₂. CO was the only C₁ product detected under either condition. CO yield agrees reasonably well with OA conversion, except during the first 5 h TOS under H₂, when excess CO production was observed. Initial selectivities to *n*-heptane were >95% and >97% under 10% H₂ and H₂, respectively, and declined by 2–3% during the first 9–10 h TOS. After 10 h TOS under H₂, OA conversion had begun to level off, and the feed composition was changed to 10% H₂. Conversion and CO yield declined immediately and appeared to be trending toward the values obtained by the

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Fig. 9. (a) OA conversion, *n*-heptane selectivity, and CO₂ selectivity; and (b) CO and CO₂ yields with TOS over Pd/C (B) at 260 °C and 1 atm (typ. OA feed conditions, H₂ mole percentage as indicated).



Fig. 10. OA conversion, CO yield and *n*-heptane selectivity with TOS over Pd/C (C) at 260 °C and 1 atm (typ. OA feed conditions, H_2 mole percentage as indicated). Data from separate experiments beginning with fresh catalyst under H_2 and 10% H_2 .

catalyst that was brought on stream under 10% H₂. Selectivity to *n*-heptane increased slightly after the change in feed composition.

3.6. WGS Reaction

Pd/SiO₂ (A) and Pd/C (A) were tested for WGS activity at 260 and 300 °C. Both catalysts were active; CO conversions obtained under each test condition are given in Table 2. At 260 °C with a 1:1 H₂O to CO ratio, the catalysts had similar activities under He. CO conversion over Pd/SiO₂ (A) decreased markedly under 10% and 75% H₂, indicating that H₂ inhibits the forward WGS reaction. The rate of the reverse WGS reaction should be negligible under these conditions, because these CO conversions are far from equilibrium. In contrast, CO conversion over Pd/C (A) remained approximately constant or increased slightly with increasing H₂ partial pressure. CO conversion increased to 300 °C.

Because of its much higher CO₂ selectivity in OA deoxygenation, a more detailed kinetics investigation of the WGS reaction was conducted over Pd/C (A). Decreasing the inlet CO and H₂O partial pressures by a factor of 2 (at constant CO space velocity and 1:1 H₂O:CO ratio), resulted in a 35% decrease in conversion. When the H₂O:CO molar ratio was increased from 1:1 to 2:1 under 10% H₂ at 260 °C, CO conversion increased proportionally. Similar behavior was observed at 300 °C under He and under 10% H₂ (Table 2). A further increase to 4:1 H₂O:CO resulted in a less than proportional rise in CO conversion. WGS reaction rates determined under differential conversion conditions (~10% or less) over Pd/SiO₂ (A) and Pd/C (A) at 260 and 300 °C are given in Table 3.

4. Discussion

4.1. Pd/SiO₂

OA deoxygenation to *n*-heptane over Pd/SiO_2 occurs via DCN, as reported previously [16]. Two reaction pathways are identified: direct DCN of OA (Eq. (2)) followed by HY of 1-heptene (Eq. (3)) and indirect DCN involving initial HDO of OA. OA HDO produces octanal as a primary product:

$$C_7H_{15}COOH + H_2 \rightarrow C_7H_{15}CHO + H_2O$$
 (5)

Subsequently, octanal undergoes DCN to *n*-heptane:

$$C_7 H_{15} CHO \rightarrow C_7 H_{16} + CO \tag{6}$$

Both DCN pathways are evident over Pd/SiO₂ (A) at 260 °C under 10% H₂. Octanal and 1-heptene yields increase concurrent with catalyst deactivation, supporting their assignments as primary products. H₂ partial pressure has large positive effects on OA deoxygenation rate and *n*-heptane selectivity over Pd/SiO₂ (A). Under H₂ at 260 °C, OA conversion approaches 100% with >95% *n*-heptane selectivity; additional minor products (1octanol and *n*octane) result from sequential HY and HDO reactions:

$$C_7H_{15}CHO+H_2 \to C_8H_{17}OH$$
 (7)

$$C_8H_{17}OH + H_2 \rightarrow C_8H_{18} + H_2O$$
 (8)

Higher H₂ partial pressures should favor HDO and increase HY rates (*e.g.*, of 1-heptene to *n*-heptane). Moreover, octanal and 1-heptene selectivities are greater at 245 °C under 10% H₂. Octanal is the only significant minor product detected at 245 °C under H₂. In contrast, under equivalent testing conditions, Pd/SiO₂ (B) exhibits very high *n*-heptane selectivity (>98%) and deactivates only gradually with TOS. High *n*-heptane selectivity was reported previously for a 1.78 wt.% Pd/SiO₂ catalyst prepared by incipient wetness impregnation of Aerosil 300 [16]. The greater propensity

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 Table 2

 Experimental results for WGS reaction over Pd/SiO₂ and Pd/C (A).

Catalyst	<i>T</i> (°C)	WHSV ^a (CO) (h^{-1})	H ₂ O: CO ^b	CO conversion (%)		
				Не	10% H ₂	75% H ₂
Pd/SiO ₂ (A)	260	0.094	1.0	6.5	1.5	0.8
	300		1.0	16.5	2.5	1.2
Pd/C (A)	260	0.094	1.0	5.8	5.8 ^d -6.9 ^e	7.7
			1.0 ^c	-	4.5	_
			2.0	-	11.3	_
			4.0	-	16.5	_
		0.19	1.0	2.8	3.4	_
	300	0.19	1.0	10.6	10.8	_
			2.0	21.1	19.8	_
			4.0	31.3	_	_

^a weight hourly space velocity: g CO/g catalyst/h.

 $^{\rm b}$ molar ratio in feed stream: 25 sccm 5% CO/He, 1, 2, or 4 μ L/min H₂O, 75 sccm H₂/He, except as otherwise noted.

^c molar ratio in feed stream: 25 sccm 5% CO/He, 1 μL/min H₂O, 20 sccm H₂, 155 sccm He.

^d 4 h time on stream.

e 12 h time on stream.

Table 3

Rates of WGS reaction over Pd/SiO₂ and Pd/C (A).

Catalyst	<i>T</i> (°C)	H ₂ O:CO ^a	CO consumption	CO consumption rate (mol/g/h)		
			Не	10% H ₂	75% H ₂	
Pd/SiO ₂ (A)	260	1.0	$2.2 imes 10^{-4}$	5.0×10^{-5}	2.7×10^{-5}	
	300	1.0	_	$8.4 imes 10^{-5}$	$4.0 imes10^{-5}$	
Pd/C (A)	260	1.0	$1.9 imes 10^{-4}$	$2.3 imes10^{-4}$	$2.6 imes10^{-4}$	
		1.0 ^b	_	$1.5 imes 10^{-4}$	_	
		2.0	_	$3.8 imes 10^{-4}$	_	
	300	1.0	7.1×10^{-4}	7.2×10^{-4}	_	

^a molar ratio in feed stream: 25 sccm 5% CO/He, 1, 2, or 4 μ L/min H₂O, 75 sccm H₂/He, except as otherwise noted.

 $^{\rm b}~$ 25 sccm 5% CO/He, 1 $\mu L/min$ H2O, 20 sccm H2, 155 sccm He.

of Pd/SiO₂ (A) for HDO could be a Na promoter effect [23] or an effect of its larger average Pd particle size.

4.2. Pd/C

In contrast to Pd/SiO₂, Pd supported on activated carbon exhibits significant CO₂ selectivity in OA deoxygenation to *n*-heptane, especially under 10% H₂. Pd/C (A) is known to be highly active and selective for deoxygenation of fatty acids to *n*alkanes in the liquid phase (300 °C, 15 atm, 5–10% H₂) with high CO₂ selectivity [8–11]. Pd/C (B) has higher initial OA deoxygenation activity than Pd/C (A) under H₂ (compare Figs. 5 and 9) consistent with its higher dispersion; however, the performance of Pd/C (A) under 10% H₂ is superior to Pd/C (B) in every aspect: activity, stability and CO₂ selectivity. Pd/C (A) and Pd/C (B) have very similar BET surface areas and micropore volumes; however, Pd/C (A) contains Na that may act a catalyst promoter, and Pd/C (B) has a much smaller average Pd particle size.

Because of its high CO₂ selectivity under 5–10% H₂, Pd/C (A) was tested for OA deoxygenation activity under He. The dominant OA reaction pathway over Pd/C (A) at 260 °C under He is DCN to 1-heptene (Eq. (2)); however, initial conversion is very low, and the catalyst deactivates rapidly. Only very small yields of CO₂ and *n*heptane are produced. Quantum chemical calculations indicate that deoxygenation of alkyl carboxylic acids on Pd(111) (via DCN or DCX) involves α carbon dehydrogenation prior to $-CH_x$ –CO₂ or $-CH_x$ –CO bond scission [17,18]. Under an inert atmosphere, loss of adsorbed H via H₂ desorption likely results in accumulation of alkylidene and alkylidyne surface species resulting in low activity and rapid catalyst deactivation. Some OA deoxygenation activity was recovered by changing the feed gas from He to 10% H₂ after >10 h TOS. Under 10% H₂, the heavily deactivated catalyst had minimal activity but high selectivity to *n*-heptane and CO.

Carbon surface properties strongly influence the fatty acid deoxygenation performance of Pd/C catalysts. For example, basic pH (either intrinsic or as altered by the presence of alkali promoters) [3] and support polarity (arising from oxygen-containing surface functional groups) [24] are factors that enhance the activity of Pd/C catalysts for liquid-phase stearic acid deoxygenation under an inert (H2-free) atmosphere. In order to better understand support effects in gas-phase OA deoxygenation, a 5 wt.% Pd/C catalyst was prepared using a high-purity, non-microporous carbon black [Pd/C(C)]. The acetylene carbon black was used without pretreatment; hence, it should incorporate a relatively low density of O-containing surface functional groups [25,26]. Moreover, the dispersion of Pd/C (C) is comparable to that of Pd/C (A). Pd/C (C) exhibited similar OA deoxygenation performance to Pd/SiO₂ catalysts prepared using Aerosil 300, especially an 1.78 wt.% Pd/SiO₂ catalyst reported previously [16]. CO₂ selectivity was negligible; H₂ partial pressure had a strong positive effect on initial deoxygenation rate; and the catalyst deactivated rapidly under H₂. This result suggests that (as in the liquid phase) carbon support polarity and the presence of alkali metals (resulting in high surface pH) are important factors affecting catalyst performance.

4.3. WGS reaction

Because Eqs. (2), (3), and (4) can be summed to give Eq. (1), OA DCX over Pd/C could result from DCN + WGS/HY (indirect DCX pathway). Moreover, Pd/C catalysts for OA deoxygenation exhibit decreasing CO₂ selectivity with TOS that could be attributed to loss of WGS activity. If the WGS reaction were fast and approached equilibrium under the conditions of OA deoxygenation over Pd/C (A), the indirect DCX pathway might account for the high CO₂ selectivities observed at low H₂ partial pressures (Fig. 7). CO₂ selectivities over Pd/C (A) at higher H₂ partial pressures, however, are much lower than predicted assuming WGS equilibrium; therefore, the

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forward rate must be inhibited under these conditions. The increase in CO_2 selectivity with temperature observed over Pd/C (A) also argues against the equilibrium assumption, since the WGS reaction is exothermic. The kinetics of the WGS reaction over Pd/SiO₂ (A) and Pd/C (A) under conditions similar to those employed for OA deoxygenation are discussed below.

The Pd/SiO₂ (A) exhibits WGS activity at 260 and 300 °C; however, the measured rates are very low (Table 3). A conservative estimate of the rate under He at 300 °C (5.5×10^{-4} mol/g/h) is comparable to that reported for a 1 wt.% Pd/SiO₂ catalyst using CO and H₂O partial pressures of 24 and 22 Torr, respectively [27]. The forward WGS reaction over Pd/SiO₂ (A) is strongly inhibited by H₂. Inhibition of the WGS reaction by H₂ has been reported for Pd supported on ceria under similar reaction conditions; however, the underlying reason for this behavior was not elucidated [27].

WGS rates over Pd/C (A) and Pd/SiO₂ (A) are equivalent at $260 \degree C$ under He (1:1 H₂O:CO molar ratio). For Pd/C (A), the turnover frequency (TOF) calculated from the measured rate at 300 °C under He is $2.15 \times 10^{-3} \, \text{s}^{-1}$. This value is about one order of magnitude lower than reported for a 1 wt.% Pd/Al₂O₃ catalyst at 300 °C albeit using much higher partial pressures of CO and H₂O (24.3 and 31.4 kPa, respectively) [13]. The apparent activation energy is 18.7 kcal/mol—within the expected range for supported Pd [13]. Significantly, H₂ does not inhibit the forward WGS reaction over Pd/C (A). In fact, the reaction exhibits a small positive order in H_2 at 260 °C. The available rate data (Table 3) at 260 °C under 10% H_2 are consistent with reaction orders of \sim 0 and \sim 0.7 for CO and H₂O, respectively. The WGS results establish that both Pd/SiO₂ (A) and Pd/C (A) are active under conditions closely approximating those prevailing during OA deoxygenation; however, under 10% H₂, the WGS activity of Pd/C (A) is \sim 5 times higher than Pd/SiO₂ (A) at 260 °C and ~9 times higher at 300 °C. The higher WGS activity of Pd/C (A) under 10% H₂ may explain, in part, its much higher CO₂ selectivity in OA deoxygenation, but WGS activity alone cannot account for the observed support effect. The rate of the WGS reaction over Pd/C (A) at 260 °C with a 1:1 H₂O:CO ratio is only 2.3×10^{-4} mol/g/h, whereas the average OA deoxygenation rate (a conservative estimate for typical reaction kinetics) under these conditions is 2.7×10^{-3} mol/g/h-more than an order of magnitude higher. A similar comparison of rates at 300 °C supports the same conclusion: the forward WGS reaction is too slow to account entirely for the high CO₂ selectivities observed in OA deoxygenation over Pd/C (A).

4.4. Summary of reaction pathways

Fig. 10 illustrates reaction pathways for OA deoxygenation to *n*-heptane over supported Pd. OA deoxygenation occurs via DCN with 1-heptene and octanal as intermediate products over Pd/SiO₂. The indirect DCN pathway proceeding via HDO to octanal is observed for OA deoxygenation over Pd/SiO₂ (A). HDO is enhanced by H₂ pressure, and 1octanol and *n*-octane are observed as minor products under H₂ at 260 °C. We infer that OA deoxygenation occurs mainly via direct DCN over Pd/SiO₂ (B) and Pd/C (C); *n*-heptane selectivity (due to sequential HY of 1-heptene) is high (>98% and >95%, respectively) and declines only marginally with TOS.

Pd supported on activated carbon has DCX and DCN activity at 235–300 °C under 10% H₂. Pd/C (A) Exhibits 75% initial CO₂ selectivity at 300 °C under 10% H₂, consistent with the performance of Pd/C (A) in liquid-phase deoxygenation of fatty acids [8–11]. The results evidence that direct DCX and DCN + WGS/HY are the main reaction pathway(s) leading to *n*-heptane and CO₂. The CO₂ selectivity (~33%) of Pd/C (A) under H₂ at 300 °C is significantly greater than calculated assuming WGS equilibrium under these conditions (21.4%), implying the existence of a direct DCX pathway. Moreover, DCN + WGS/HY cannot account entirely for the high CO₂ selectiv-



Fig. 11. Reaction pathways in OA deoxygenation to *n*-heptane over supported Pd.

ity of Pd/C (A), because the forward WGS reaction is too slow. At higher H₂ partial pressures, OA deoxygenation is inhibited and CO₂ selectivity is markedly lower. The simultaneous losses of overall activity and CO₂ selectivity are traceable to lower DCX activity. Higher partial pressures of H₂ favor DCN; however, the increase in DCN activity does not compensate the loss of DCX activity. These results are consistent with H₂ and CO inhibition of the DCX pathway, as previously observed in liquid-phase deoxygenation of stearic acid over Pd/C (A) [9]. Under H₂ at 260 °C, CO₂ selectivity is nearly zero, *n*-heptane selectivity is lower, and HDO products (octanal, 1-octanol, *n*-octane) are formed. Apparently, DCN via an aldehyde intermediate is favored over Pd/C under a hydrogen-rich atmosphere, as reported by Rozmyslowicz, et al. [28] for lauric acid deoxygenation in the liquid phase. Multiple experiments evidence that CO₂ selectivity over Pd/C (A) increases with temperature, consistent with higher activation energy for DCX than for DCN (Fig. 11).

5. Conclusions

Pd-catalyzed DCX and DCN are parallel pathways that are sensitive to the catalyst support, promoters (e.g., Na), and reaction conditions (temperature, H₂ partial pressure). OA deoxygenation occurs via DCN with 1-heptene and octanal as intermediate products over Pd/SiO₂. In contrast, Pd supported on activated carbon exhibits DCX and DCN activity. Low H₂ partial pressures (5–10%) increase deoxygenation activity and CO2 selectivity over Pd/C (A), whereas higher H₂ partial pressures inhibit DCX and promote DCN. In the absence of H₂, Pd/C (A) initially has very low initial deoxygenation activity and deactivates rapidly with TOS. We infer that the presence of adsorbed H favors hydrogenation of surface alkenyl and alkyl groups avoiding rapid catalyst deactivation. The much greater WGS activity of Pd/C (A) than Pd/SiO₂ (A) under H₂ can account partially for its higher CO₂ selectivity in OA deoxygenation, but WGS activity alone cannot explain the observed support effects. The higher Na content of Pd/C (A) may explain its higher CO₂ selectivity and lower deactivation rate relative to Pd/C (B). Pd supported on high-purity acetylene carbon black exhibits only DCN activity under these conditions, indicating that support polarity (arising from oxygen-containing surface functional groups) also influences the OA deoxygenation performance of Pd/C catalysts.

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