ABSTRACT

SUN, KEYI. Catalytic Deoxygenation of Fatty Acid to Hydrocarbon Using Supported Palladium and Palladium-Gold. (Under the direction of Harold Henry Lamb).

Catalytic deoxygenation of fatty acids (FAs) to hydrocarbons using supported Pd catalysts is a key enabling technology in lipid biomass conversion to "drop-in" replacements for petroleum-derived transportation fuels; however, the kinetics and mechanism(s) of FA deoxygenation and the catalyst deactivation mechanism are not well understood. In this work, vapor-phase catalytic deoxygenation of octanoic acid (OA) was investigated over silica- and carbon-supported Pd catalysts at 245-300°C and 1 atm using a fixed-bed micro-reactor with on-line product analysis. A commercial 5 wt. % Pd/SiO₂ catalyst was found to be active for OA decarbonylation via a reductive pathway involving octanal as an intermediate. OA conversion and selectivity to n-heptane increased with increasing temperature and hydrogen partial pressure. Under equivalent experimental conditions, a commercial 5 wt. % Pd/C catalyst was found to be more active (>95% OA conversion) and exhibit much greater CO₂ selectivity (65%). With this catalyst, increasing H₂ partial pressure inhibited OA decarboxylation and promoted decarbonylation; octanal and octanol were detected only under hydrogen-rich conditions. Moreover, this catalyst had water-gas-shift (WGS) activity under OA deoxygenation conditions. Plausible reaction pathways for OA deoxygenation are proposed based on the experimental results.

OA deoxygenation was investigated further using lab-prepared Pd/SiO₂ and PdAu/SiO₂ catalysts. A 1.78 wt. % Pd/SiO₂ catalyst with an average Pd particle size of 7.5 nm and a broad size distribution was prepared by incipient wetness, and a 0.6 wt. % Pd/SiO₂ catalyst containing 1.5-nm particles with a narrow size distribution was prepared by ion exchange. The catalysts
were characterized by CO chemisorption, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and high-resolution transmission electron microscopy (HRTEM). The larger supported nanoparticles exhibited well-defined surface facets that adsorbed CO preferentially at 2-fold bridging sites. The smaller supported nanoparticles exhibited strong linear and bridging v_{CO} bands. The 0.6 wt. % Pd/SiO_{2} catalyst had initial OA deoxygenation activity, but deactivated rapidly and irreversibly with time on stream. In contrast, the 1.78 wt. % Pd/SiO_{2} catalyst deactivated less rapidly and could be regenerated by heating in H_{2} to remove OA residues. The catalyst deactivation mechanism was inferred to be self-poisoning by OA and CO. PdAu/SiO_{2} catalysts were prepared that contained 4-5 nm supported alloy nanoparticles. Alloying Pd with Au was found to improve catalyst stability without significantly reducing deoxygenation activity by reducing the CO adsorption energy and mitigating self-poisoning by OA (and related species).

Liquid-phase catalytic deoxygenation of stearic acid (SA) to \( n \)-heptadecane (\( n \)-C_{17}) was investigated over a series of carbon-supported Pd catalysts at 300ºC and 15 atm using a semi-batch stirred autoclave reactor with on-line gas analysis by quadrupole mass spectrometry. Commercial 5% Pd/C catalysts and in-house prepared 5% Pd/C (activated carbon, AC) and 5% Pd/CB (carbon black, CB) catalysts were screened under He and 5% H_{2} (balance He). The Pd/C catalysts were characterized by CO chemisorption, slurry pH measurements, temperature-programmed desorption (TPD), and elemental analysis. All the commercial Pd/C catalysts and the lab-prepared Pd/AC catalyst exhibited catalytic activity under He; however, Na- and K-rich catalysts with basic slurry pH values and higher CO_{2} TPD peak areas had higher \( n \)-heptadecane yields and CO_{2} selectivities. In contrast, the lab-prepared Pd/CB catalyst had negligible activity under He. SA deoxygenation activity under He was
inferred to be related to spillover hydrogen generated by \textit{in situ} reduction of Pd/AC catalysts. Under flowing 5\% H\textsubscript{2}, the Pd/AC catalysts exhibited high SA conversions and high CO\textsubscript{2} selectivities; Pd/CB was active for SA decarbonylation under these conditions.
Catalytic Deoxygenation of Fatty Acid to Hydrocarbon Using Supported Palladium and Palladium-Gold

by
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Catalytic Deoxygenation of Octanoic Acid over Carbon- and Silica- Supported Pd Catalysts

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Literature Review of Catalytic Deoxygenation of Fatty Acids

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1. Background

The availability of energy resources is of paramount importance to society, and there has been an enormous increase in the global demand for energy in recent years as a result of industrial development and population growth. The huge demand of energy, especially liquid fuels, and diminishing of oil reserves has caused a scarcity of conventional energy resources. Peak oil production has been estimated to occur anywhere from the year 2000 to 2037 [1-3]. By 2030, global energy consumption is projected to grow by 36% and demand for liquid transport fuels will have risen by 16 million barrels more a day [4]. We know that the energy production and use contribute to global greenhouse gas emissions, and in order to meet the challenges of rising energy demand whilst reducing CO$_2$ emissions, more widespread use of alternative (bio-renewable) energy sources is required. Biofuels offer a way to produce transportation fuels from renewable sources and to reduce net CO$_2$ emissions because the CO$_2$ emitted during combustion of the fuel is captured during the growth of the feedstock [5]. Biofuels as important alternatives to liquid transportation fuel came into very public prominence in 2005, and the Energy Policy Act of 2005 established the first mandate for biofuels production in US history [6]. After 3 years, 9 billion gallons of ethanol were to be blended into existing fuel in 2008 [7] and biodiesel production increased from 25 to an estimated 700 million gallons [8].

First-generation biofuels, bioethanol and biodiesel, are widely known as substitutes for their fossil counterparts, gasoline and diesel. Bioethanol produced by fermentation of sugars derived from cereal grains (e.g., wheat, corn) and sugarcane is the most common biofuel worldwide, particularly in Brazil. The history of bioethanol in Brazil dates from the 1970s and
is related to sugarcane cultivation. From 2004 to 2011 Brazilian fuel ethanol production increased from 3989 million gallons to 5573 million gallons. Global fuel ethanol production reached 23 billion gallons in 2010, and the United States was the world’s largest producer at 13.2 billion gallons.[9]

Even though ethanol for fuel has already been successfully commercialized, it still has some disadvantages. First, ethanol in the US is mainly produced from corn; therefore, this method threatens food supplies and biodiversity and yields a very poor energy return on investment (EROI) between 0.75 and 1.4 [10,11]. Figure 1 shows the trend in nominal price terms of corn and the cost of imported crude oil. Except the corn price peak in 1995 because of the weather extremes, corn prices climbed up very rapidly from 2006 to 2008 due to the increased demand for biofuel grain. The US government is engaged in vast subsidies on agricultural commodities in general and especially for bioethanol.

Figure 1. Corn and imported crude oil prices. Sources: USDA and EIA
Second, due to its lower energy density, immiscibility with hydrocarbons, and corrosive properties, ethanol can be destructive to engine components and cannot be considered as a drop-in replacement for petroleum-based fuels [3].

Biodiesel consists of fatty acid methyl esters (FAME) derived from triglycerides (TG) (fats and oils) via transesterification with methanol. After FAME purification and testing, the product can be used as a drop-in replacement for diesel fuel (B100) or be blended with diesel with 10 or 20%. The most common blend of U.S. biodiesel is 20% biodiesel with 80% petroleum diesel (B20) [12]. However, biodiesel has many undesirable physical and chemical properties such as its high viscosity, high cloud point temperature, poor oxidation stability, and lower energy density. [13, 14] Moreover, the land requirement to replace petroleum fuel with biodiesel has been calculated to be greater than land available for these oil crops (such as soybeans) in US [15], let alone the crops price increasing problem. Clearly, biodiesel made from traditional agricultural (field) crops is not suitable for replacing petroleum transportation fuels due to the huge quantity required. Fortunately, microalgae were found to be an alternative source of TG which has greater oil yields per land area. As shown in Table 1, the oil yield of microalgae is at least two orders of magnitude greater than soybeans. The biodiesel used in US is primarily produced from soybean oil [5].

Considering these limitations, second-generation biofuels has been developed to produce “drop-in” transportation fuel replacements. By deoxygenating TG, the resultant hydrocarbons can undergo traditional petroleum refining processes to generate fuels identical to current gasoline and diesel. There are two potential methods for generating hydrocarbons from fats
and oils from biological sources: hydrodeoxygenation (HDO) of TG and catalytic
deoxygenation (decarboxylation/decarbonylation) of fatty acids (FAs).

Table 1. Oil yields from various terrestrial crops and microalgae.[13]

<table>
<thead>
<tr>
<th>Crop</th>
<th>Oil yield (L/ha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corn</td>
<td>172</td>
</tr>
<tr>
<td>Soybean</td>
<td>446</td>
</tr>
<tr>
<td>Canola</td>
<td>1190</td>
</tr>
<tr>
<td>Jatropha</td>
<td>1892</td>
</tr>
<tr>
<td>Coconut</td>
<td>2689</td>
</tr>
<tr>
<td>Oil palm</td>
<td>5950</td>
</tr>
<tr>
<td>Microalgae</td>
<td>58,700</td>
</tr>
</tbody>
</table>

Hydrodeoxygenation (HDO) is a hydrogenolysis process for removing oxygen heteroatoms from organic molecules via the addition of hydrogen across C-O bonds, ultimately producing hydrocarbons and water. Typical HDO catalysts are nickel or cobalt on alumina support [16, 17], and reaction conditions are 260-400°C under high H₂ pressure.

A scheme illustrating hydrodeoxygenation of triglycerides in Scheme 1.
Scheme 1. Hydrodexoxygenation of triglycerides to yield hydrocarbon products.

In this reaction, a minimum 12mol of H\textsubscript{2} is required to yield alkane from triglycerides. The need of H\textsubscript{2} as a reactant and high reaction pressure limits the economic feasibility of TAG hydrodeoxygenation to alternative transportation fuel. However deoxygeantion of free fatty acids (FFAs) using Pd support catalyst does not need H\textsubscript{2} to produce hydrocarbon as shown in Scheme 2.

Scheme 2. FAs and glycerol are generated by the hydrolysis of triglycerides (1). Hydrocarbons are then produced via decarboxylation (2) and decarbonylation (3) of FAs.
First, TG are hydrolyzed to 3 moles FA and 1 mol of glycerol per mol. Subsequently, FAs are then catalytically deoxygenated to yield alkanes and a mixture of CO and CO$_2$. These alkanes then can be isomerized and cracked to obtain the right distribution of compounds required for gasoline, jet fuel, and diesel fuel applications. Roberts, et al. invented the 4-step biofuels process shown in Figure 2 that employs this approach [18]. A microalga *Dunaliella* is a preferred source of TG for the process, because it can double its biomass every 30 hours and because it has a cell membrane instead of a cell wall, making it easier to extract lipids from the cells. Our research is focused on catalytic deoxygenation of FAs using supported Pd catalysts.

Figure 2. A four-step process that converts animal fats and plant oils into “drop-in” hydrocarbon fuels, with glycerol by-product used to provide thermal energy for the process.

FA deoxygenation can be achieved by either decarboxylation or decarbonylation. The stoichiometric equations are displayed below [19]:

$$C_{n}H_{2n+1}COOH \rightarrow n-C_{n}H_{2n+2} + CO_{2} \quad \text{(Decarboxylation)}$$
In decarboxylation, the carboxylic acid functional group is removed as CO$_2$, yielding a linear hydrocarbon ($n$-alkane).

$$C_nH_{2n+1}COOH \rightarrow n-C_nH_{2n} + CO + H_2O \quad \text{(Decarbonylation)}$$

Decarbonylation yields CO, H$_2$O and an alkene (unsaturated hydrocarbon). The alkene may subsequently be saturated by hydrogenation to form an $n$-alkane. The decarboxylation pathway is preferred, because obviates the additional cost of hydrogen and avoids the generation of CO, a catalyst poison. The advantages of catalytic deoxygenation are lack of H$_2$ consumption and relatively low pressure operation compared HDO.

2. FA deoxygenation in the liquid phase

Several research groups have performed FA deoxygenation research. Snåre, a member of Murzin’s group, published a liquid-phase catalyst screening paper in 2006 [19]. Several transition metals (Ni, NiMo, Ru, Pd, PdPt, Pt, Ir, Os, and Rh) on various metal oxides and carbon supports were tested for stearic acid (SA) deoxygenation in a 300-ml semi-batch stirred autoclave reactor. The reaction conditions were 6 bar, 300 °C, 86 g dodecane, 4.5 g SA (0.154 mol/L), under 25 ml/min flowing He for 6 h. In this paper, 5 wt. % Pd/C was the most successful catalyst displaying 100% conversion and 95% selectivity toward $n$-heptadecane under an inert purge. Unfortunately, rapid catalyst deactivation is observed under the inert atmosphere. After that Snåre et al also conducted semi-batch and fed-batch work on oleic acid and linoleic deoxygenation over 5 wt.% commercial Pd/C [20]. It was found that hydrogenation of oleic acid to stearic acid (SA) prior to SA deoxygenation. Under an inert environment, it was found very low activity on oleic acid deoxygenation, thus maintaining a low H$_2$ consumption per mole alkane formed is essential for this process. Murzin, et al. also
studied various 5 wt% Pd/C catalysts for the deoxygenation of stearic acid and its ester (ethyl stearate). They studied catalyst acidity, type of feed, effect of solvent, and gas atmosphere and found that the gas atmosphere and the acidity of catalysts were important factors in determining liquid product selectivity. SA deoxygenation over the most alkaline Pd/C catalyst under a H₂ atmosphere gave the highest yields and initial deoxygenation rates, as well as the highest selectivity to n-heptadecane.[21] They proposed the reason for higher selectivity to n-heptadecane over alkaline catalysts was the capability of SA to react further over such basic catalysts is stronger than acidic catalyst. The drawback to using alkaline Pd/C catalysts was the substantial formation of aromatic side products. The effect of Pd dispersion on deoxygenation of palmitic and stearic acid mixtures over 4 lab-prepared 1 wt% Pd on Sibunit carbon catalysts was investigated in a semi-batch reactor [22]. Different metal dispersions were achieved by precipitation deposition of Pd chloride solutions over a pH range (8-10). The Pd dispersions was determined by CO chemisorption to be 18%, 47%, 65% and 72%; the catalysts with dispersions of 47% and 65% were the most active catalysts with highest TOF. However, since the different metal dispersions were achieved by changing the pH of the palladium precursor solution, along with Pd dispersion, the acidity of catalysts also changed. According to the previous reference, alkaline Pd/C has higher catalytic activity for SA and ethyl stearate deoxygenation; therefore, it is hard to rule out the effect of pH. Moreover, their TEM mean particle size results do not agree well with their CO chemisorption measurements. Going by the TEM results, highest Pd dispersion catalyst had similar particle size with medium (optimum) Pd dispersion, making it hard to draw a concrete conclusion.
Besides Murzin’s group, Lamb’s group at NCSU (our group) has also performed significant research on catalytic deoxygenation of FAs. Several 5% Pd/C commercial catalysts, Pd/Al₂O₃, and Pd/SiO₂ were screened under flowing 0, 5, and 10% H₂ in SA deoxygenation [23]. Commercial Pd/C (E117) had the best performance under all those conditions with high conversion and very high CO₂ selectivity. Under He, the other catalysts failed to achieve 100% SA conversion due to rapid deactivation. All of the catalysts were far more stable under H₂ yielding high SA conversion and n-heptadecane yield but differing CO₂ selectivities. Parametric studies were also conducted in the semi-batch and fed-batch experiments. Increasing initial SA concentration, increasing H₂ partial pressure, and presence of CO were shown to inhibit decarboxylation. However, under conditions of strong decarboxylation inhibition, the decarbonylation rate was unaffected; therefore, Immer, et al. inferred that decarboxylation occurs over different catalytic sites than decarbonylation. Fed-batch deoxygenation of SA and oleic acid was demonstrated in a 50-mL stirred autoclave reactor with continuous feeding for up to 24 h [24]. When higher H₂ partial pressures were employed, a switchover in product selectivity from CO₂ to CO was observed. Immer proposed that switchover phenomenon arose from H₂ inhibition of the decarboxylation pathway resulting in SA accumulation. SA accumulation increases the decarbonylation rate leading to further inhibition of the decarboxylation pathway by CO.

The most active Pd/C catalyst was used to investigate the influence of alkyl chain length on deoxygenation kinetics for C8-C18 fatty acids [25]. It was found that as FA carbon number decreases, reaction time and H₂ consumption increase, and CO₂ selectivity and initial
decarboxylation rate decrease. The increase in initial decarboxylation rates for longer chain FAs is attributed to their greater propensities for adsorption on the activated carbon support.

3. FA deoxygenation in vapor phase

Maier, et al. studied the decarboxylation of carboxylic acids in the vapor phase over Ni/SiO$_2$ and Pd/SiO$_2$ [26]. The reaction temperature for Ni catalyst was 180 °C and for Pd catalyst was 330 °C. Both catalysts were operated under 25mL/min H$_2$ at atmospheric pressure. Heptanoic acid and octanoic acid deoxygenation over Pd/SiO$_2$ resulted in high yields of hexane and heptane, 98% and 97%, respectively. In contrast, over Ni/SiO$_2$, the yields of hexane and heptane were 26% and 64%, respectively. Maier, et al proposed a tentative mechanism for carboxylic acid decarboxylation. Decarboxylation of primary carboxylic acids over Pd/SiO$_2$ involved with an α, β-adsorbed carboxylate intermediate (Scheme 3) that subsequently undergoes C-C bond cleavage.

![Scheme 3. α, β-adsorbed carboxylate intermediate](image)

More recently, Boda, et al, studied catalytic hydroconversion of tricaprylin and caprylic acid (octanoic acid) in the vapor phase over Pd/C and Ni,Mo/γ-Al$_2$O$_3$.[27] The reaction was carried out in a high-pressure flow reactor at 300°C-400 °C. Tricaprylin conversion was found
to proceed in consecutive steps: hydrogenolysis of tricaprylin to caprylic acid and propane followed by deoxygenation of the caprylic acid intermediate. Caprylic acid decarbonylation to heptane over Pd/C was proposed to pass through a formic acid intermediate which subsequently decomposed to CO and H\textsubscript{2}O in the presence of H\textsubscript{2}.

4. Bimetallic catalysts

Bimetallic catalysts have attracted great attention because of their enhanced catalytic stabilities, activities and selectivities, as compared with their single-metal constituents. [28]. Among the various bimetallic materials, Pd-Au has been intensively investigated and employed as catalyst for many important applications such as vinyl acetate (VA) synthesis [29], low temperature CO oxidation [30], formic acid decomposition [31], and aldehyde preparation from alcohol oxidation [32]. This enhancement of catalytic stabilities, activities and selectivities is often caused by two alloy effects: geometric (ensemble) and electronic (ligand) [32].

Figure 3. The effect of replacing Pd atoms with Au in the Pd (111) surface on the activation barrier for C-H bond activation of surface-bound acetate.
Neurock, et al. examined the structure sensitivity of acetic acid decomposition using density functional theory (DFT) calculations by replacing Pd atoms in the Pd (111) surface with Au to establish the effects on the activation barrier for acetate decomposition [23] (Figure.3). The results showed that the Pd(111) surface has lowest barrier for C-H bond activation at +150kJ/mol. By exchanging a Pd atom which is not directly involved in the adsorbate-surface complex, but is the first nearest neighbor with Au, the barrier is increased to +167kJ/mol. This suggests that the electronic (ligand) effect is relatively weak. When a Pd atom that is directly involved in the adsorption complex was substituted, the barrier is increased by +100kJ/mol to +250kJ/mol. Also, the effect of alloying Pd with Au in acetoxylation of ethylene to vinyl acetate has been investigated experimentally [34]. It was concluded that role of Au is to isolate single Pd sites that facilitate the coupling of critical surface species to product, while inhibiting the formation of undesirable reaction byproducts. The effect of Au in these two reactions is primarily a geometric one. In our OA deoxygenation system, the effect of alloying Pd with Au has not been established.

5. **Surface reaction mechanisms of decarboxylation and decarbonylation**

In order to obtain a better understanding of the elementary steps involved in catalytic deoxygenation of FAs, computational modeling methods have been used. Heyden, et al, investigated DCX and DCN mechanisms of propanoic acid on Pd (111) using DFT calculations [35]. They proposed the most kinetically favorable pathway in the decarboxylation (DCX) mechanism involves first O-H scission of acid group, followed by C-COO cleavage or possibly fully dehydrogenation of α-carbon to produce CH₃C COO prior to C-COO scission since the barrier activation energy of this two possible pathway are about the same. The most kinetically
favorable decarbonylation (DCN) pathways involved α- and β-carbon dehydrogenation prior to C-C bond scission because of the barrier energy of direct DCN is too high. Thus, α- and β-carbon dehydrogenation facilitates DCN, and the initial dehydrogenation step becomes rate-limiting. Overall, the activation barriers for the DCX pathway seem to be higher than the barriers along the DCN pathway.

Lamb, et al. [36] used configuration interaction theory to investigate decarboxylation of butanoic acid on the (111) surface of a Pd₄₂ nanoparticle. They proposed reaction of Pr-COO (ads) and H (ads) resulted in direct decarboxylation with barrier activation energy of 104 kJ/mol. Also adsorbed H was found to influence the reaction barrier and reference energies for surface intermediates by competing with O for Pd electrons. For example, with adsorbed H, C₂H₅-CH-COO (ads) leads to CO₂ and propyl with 32 kJ/mol, which is lower than C₂H₅-CH-COO (ads) to propylidene 75 kJ/mol. The energy of butanoic acid adsorption on Pd surface increases from 43 to 109 in the present of adsorbed H, compensating for the lower decomposition barrier.
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Catalytic Deoxygenation of Octanoic Acid over Carbon- and Silica – Supported Pd Catalysts

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Abstract

Vapor-phase catalytic deoxygenation of octanoic acid (OA) was investigated over silica- and carbon-supported Pd catalysts at 245-300 °C and 1 atm using a fixed-bed micro-reactor with on-line gas chromatography. A commercial 5 wt.% Pd/SiO₂ catalyst (BASF Escat 1351) was found to be active for OA decarbonylation via a reductive pathway involving octanal as an intermediate. Conversion and selectivity to n-heptane increased with increasing temperature and hydrogen partial pressure. 5% Pd on non-porous carbon black support demonstrated decarbonylation activity as well. Under equivalent experimental conditions, a commercial 5 wt.% Pd/C (Evonik E117) catalyst was found to be most active and only one catalyst has water gas shift activity, indicating a strong support effect for this reaction. At 260°C under 10% H₂, OA conversion was >95% with 99% n-heptane selectivity and 65% CO₂ selectivity. Increasing H₂ partial pressure resulted in a decrease in OA conversion and CO₂ selectivity. A second 5 wt.% Pd/C catalyst (AA38300) exhibited less active than E117 but still selective to decarboxylation pathway. Through kinetic study OA deoxygenation was diagnosed as first order reaction and the initial TOF over Pd/C E117 was 0.027s⁻¹. The influence of hydrogen partial pressure on conversion and selectivity was investigated over Pd/C (E117). The reaction intermediates (octanal and octanol) were performed over Pd/C under H₂ at atmospheric pressure. Possible reaction pathways were discussed according to different catalysts and reaction atmosphere.
1. Introduction

Increasing petroleum prices combined with environmental concerns are causing our society to search for new, renewable sources of liquid transportation fuels (biofuels). First-generation biofuels (bioethanol and biodiesel) are widely known as substitutes for their petroleum-derived counterparts, gasoline and diesel. Due to their drawbacks: “food-for-fuel” competition, nitrous oxide emissions [1], poor oxidation stability and lower energy density [2,3], second-generation hydrocarbon biofuels are expected to supplant them. With the advent of algal oils technology, large quantities of fatty acids (FAs) can be produced using minimal farmland to provide biologically derived transportation fuels for the future [4]. Hydrocarbons for biofuels can be produced by catalytic deoxygenation of fatty acids using supported palladium catalysts [5-12]. This work focuses on the deoxygenation of octanoic acid (OA) over supported palladium (Pd) catalysts.

FA deoxygenation over Pd catalysts can occur via two pathways:

\[
\text{R-COOH} \rightarrow \text{RH} + \text{CO}_2 \quad \text{(Decarboxylation)} \quad \text{RH- alkane}
\]

\[
\text{R-COOH} \rightarrow \text{R=} + \text{H}_2\text{O} + \text{CO} \quad \text{(Decarbonylation)} \quad \text{R=-alkene}
\]

The products of decarboxylation (DCX) are \( \text{CO}_2 \) and a linear alkane with one less carbon atom. Decarbonylation (DCN) yields \( \text{CO}, \text{H}_2\text{O} \) and an alkene with one less carbon atom. \( \text{H}_2 \) is required for hydrogenation of the alkene. The DCX pathway is preferred because it eliminates the additional cost of hydrogen and generation of \( \text{CO} \), a known noble metal catalyst poison. There is a current debate as to whether the water gas shift (WGS) reaction contributes to the decarboxylation pathway. Because supported Pd is catalytically active for WGS [13,14] and
the DCN reaction can be combined with the WGS reaction and alkene hydrogenation to give the DCX pathway.

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad \text{(Water Gas Shift)}
\]

Early work by Maier, et al. [15] demonstrated that Pd on silica (Pd/SiO\(_2\)) is an active and highly selective catalyst for vapor-phase OA deoxygenation under a H\(_2\) atmosphere. In this work, OA was converted to \(n\)-heptane in 97% yield over Pd/SiO\(_2\) at 603K and 1 atm in flowing H\(_2\). In contrast, no catalytic activity was observed under an inert atmosphere although H\(_2\) does not appear in the decarboxylation stoichiometry. More recently, co-feeding H\(_2\) was found necessarily to maintain steady-state decarboxylation activity in liquid-phase stearic acid deoxygenation experiment. [12] In addition Immer, et al. studied the WGS reaction under these conditions and concluded WGS activity cannot account for the >92% CO\(_2\) selectivity observed. Boda, et al. studied OA deoxygenation over Pd/C at high pressure and concluded that in the presence of H\(_2\), the reaction occurs via DCN [16]. Their proposed decarbonylation route involves a formic acid intermediate that decomposes to CO and H\(_2\)O. A recent paper by Murzin and coworkers [17] suggests that DCN via an aldehyde intermediate is favored over Pd/C under a hydrogen-rich atmosphere.

In order to get a better understanding of the elementary steps involved in catalytic deoxygenation of fatty acids, computational modeling methods have been used extensively. Heyden, et al. investigated DCX and DCN mechanisms of propanoic acid on Pd (111) using density functional theory (DFT) calculations [18]. They demonstrated the kinetically favorable DCX pathway involves first O-H scission of acid group, followed by C-COO cleavage. The most kinetically favorable DCN pathways involved \(\alpha\)- and \(\beta\)-carbon dehydrogenation prior to
C-C bond scission because of the barrier energy of direct DCN is too high. Overall, the activation barriers for the DCX pathway seem to be higher than the barriers in the DCN pathway(s). Lamb, et al [19] used *ab initio* configuration interaction theory to investigate DCX of butanoic acid on the (111) surface of a Pd_{42} nanoparticle. They concluded adsorbed H influences reaction barrier and reference energies for surface intermediates by competing with O for Pd electrons. For example, with adsorbed H, C_{2}H_{5}-CH-COO (ads) leads to CO_{2} and propyl with 32 kJ/mol, which is lower than C_{2}H_{5}-CH-COO (ads) to propylidene 75 kJ/mol.

In this work, we systematically investigated the possible pathways for vapor-phase OA deoxygenation over Pd supported on silica, activated carbon, and carbon black. The effects of temperature and hydrogen partial pressure on deoxygenation kinetics and reaction pathways were studied. In addition, the kinetics of the WGS reaction over the Pd/C catalysts was measured.

2. Experimental Methods

2.1 Materials

OA (99%) was purchased from Fisher. Ultra-high-purity (99.99%) He, H\textsubscript{2} and 5% CO (balance He) were purchased from National Welders. Pd(NO\textsubscript{3})\textsubscript{2}.xH\textsubscript{2}O was purchased from Strem Chemicals. Commercial 5 wt.% Pd/C catalysts were purchased from Evonik-Degussa (E117), Alfa Aesar (AA38300). A 5 wt.% Pd/SiO\textsubscript{2} catalyst was purchased from Strem Chemicals (BASF Escat 1351). High purity acetylene carbon black (CB) (~200 mesh powder) was obtained from Strem Chemicals. A 5 wt.% Pd on carbon black catalyst 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 then reduced *ex situ* at 400 °C in flowing H$_2$ for 1 h.

2.2 Catalyst characterization

The specific surface area and pore volume were obtained through N$_2$ porosimetry using a Micromeritics ASAP 2020c instrument. The carbon-supported catalysts were degassed under vacuum at 300°C for 8 h before N$_2$ physisorption measurements at 77 K. The Brunauer-Emmett-Teller (BET), Barrett-Joyner-Halenda (BJH) and t-plots methods were used to determine the surface area, mesopore volume, and micropore volume, respectively. For fresh catalysts, Pd dispersion was measured by CO chemisorption using a Micromeritics 2020c instrument. After reduction at 300 ºC for 2 h, adsorbed H$_2$ was removed by 4 h evacuation at 300°C. Static volumetric CO chemisorption measurements were performed at 35°C. After the first isotherm had been measured, the sample was evacuated 35°C for 30 min prior to measuring a second isotherm. Pd dispersion calculations were based on the difference between and first and second isotherms (strongly adsorbed CO) using a CO to Pd surface atom stoichiometry of 1:1.5. For used catalysts, Pd dispersion was obtained by CO pulse chemisorption using a Micromeritics AutoChem 2920. Before CO pulse chemisorption, the sample was reduced at 300 ºC with H$_2$ for 1h then purge with He at same temperature for 30 min. The particle diameters ($d$) were calculated from the dispersion ($D$) using the equation below: [20]

$$d = \frac{1.12}{D}$$
Transmission electron microscopy (Hitachi HF2000) was used to determine particle size distributions for Pd/C (E). Explain how many particles were counted, etc.

2.3 Deoxygenation Experiments

OA deoxygenation experiments were conducted in a stainless steel tubular reactor, 0.5 in. OD using 0.5 g (typ.) catalyst powder suspended between quartz wool plugs. The catalyst temperature was measured using a Type K thermocouple in direct contact with the bed. Gas flow rate and composition to the reactor were set by mass flow controllers, and liquid OA was fed by syringe pump (ISCO Serial D) and evaporated prior to entering the reactor. Each catalyst was reduced in situ at 300 °C for 1 h in flowing H₂ (100 sccm). Typical test conditions were 4 μL/min OA, 100 sccm 10% H₂/He, 260°C and 1 atm. The H₂ partial pressure, reactor temperature, and OA weight hourly space velocity (WHSV) were adjusted, as needed, during the investigation.

WGS reaction experiments were conducted in the same stainless steel reactor using 0.5 or 1.0 g catalyst powder suspended between quartz wool plugs. Under typical reaction conditions (at 260°C and 1 atm), 1 μL/min H₂O was injected and evaporated into a stream of flowing CO (25 sccm) and 10% H₂ (balance He) (75 sccm). Reactor temperature, CO WHSV and H₂O to CO ratio were changed in the experiments.

2.4 Analytical Methods

OA and organic products in the reactor effluent were analyzed by on-line GC-FID, and gaseous products like CO and CO₂ were monitored by on-line QMS or GC-TCD. The GC-FID used 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, then increase to 240°C with 40°C/min ramping rate. The FID responses were calibrated using a series of different concentrations of OA, n-heptane, 1-heptene and octanal in suitable solvents. The GC-TCD used was a 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 SRI GC-TCD. The QMS was 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 CO₂ (48 m/z) signals were monitored routinely. The CO signals have been corrected for CO₂ electron fragmentation by subtracting 10% of the CO₂ (44 m/z) intensity. From GC and QMS data, the OA conversion, yields of heptane, heptene and octanal, and CO₂ selectivity were determined.

3. Results

3.1 Catalyst Characterization

The commercial Pd/SiO₂, Pd/C (E), Pd/C (AA) and lab-prepared Pd/CB were characterized by nitrogen porosimetry and CO chemisorption, and the results are given in Table 1. The BET surface areas of Pd/C (E) and Pd/C (AA) are 800-850 m²/g with significant microporosity (micropore volumes of 0.17-0.21 cm³/g). Pd/SiO₂ has moderate surface area, very low micropore volume, and high total pore volume. Pd/CB has the lowest surface area, because the essentially non-porous structure of the carbon black support. The Pd dispersions decrease in the order: Pd/C (A) > Pd/CB > Pd/C (A) > Pd/SiO₂. The Pd particle size of Pd/C (E) from TEM (Fig. 1), 7.2 nm average diameter, agrees very well with the estimate from CO chemisorption.
3.2 OA Deoxygenation over 5 wt.% Pd/SiO$_2$

Deoxygenation over Pd/SiO$_2$ appears to proceed strictly via the DCN pathway. OA deoxygenation under 10% H$_2$ at 260 °C yields primarily CO as evidenced by the GC-TCD in Fig. 2b. In Fig. 2a it can be seen that as the reaction progresses, OA conversion and $n$-heptane yield dropped with time on stream (TOS), and concomitantly, the 1-heptene and octanal yields increased. After 12 h, the feed stream was changed from 10% to 100% H$_2$, and OA conversion and $n$-heptane yield rapidly approached 100%. Concomitantly, the effluent concentrations of 1-heptene and octanal decreased to negligible values. Yield of CO also been plotted against yield of heptane + heptene in Fig. 2b. The near overlap of these data demonstrates that CO is produced with 1:1 ratio to the C$_7$ species.

OA deoxygenation over Pd/SiO$_2$ also was tested at different temperatures. When the reaction temperature was increased from 245, to 260, and then to 300ºC, conversion increased step by step at each temperature, as shown in Fig. 3a. At 245 °C, the octanal and heptene selectivities are 20 and 10%, respectively (Fig. 3b). The octanal selectivity drops to 8% at 260ºC and 0% at 300ºC. The heptene selectivity increases slightly at 260ºC and decreases to 0% at 300ºC.

3.3 OA Deoxygenation over 5 wt.% Pd/C (E)

Vapor-phase OA deoxygenation over Pd/C (E) was tested under He. The experimental conditions were 260 °C with 0.44 h$^{-1}$ WHSV. The yields of heptane, heptene and octanal are plotted against TOS in Fig. 4a. The CO and CO$_2$ mole fractions during the same time period are plotted in Fig. 4b. During the first 4 h, heptane, heptene and octanal were observed, with heptene in a higher concentration than heptane, which is consistent with the CO mole fraction.
was higher than CO$_2$ shown in Fig. 4b. Under He, the catalyst displayed low initial activity for OA deoxygenation in the first 4 h, and then deactivated completely. This deactivation largely is irreversible, because no significant conversion increase was observed when 10% H$_2$ was employed after 14 h TOS.

In contrast, under 10% H$_2$ the catalyst initially exhibited >95% OA conversion with 65% CO$_2$ selectivity and very low deactivation over 15 h TOS, as shown in Fig 5. The main product was n-heptane (>99%); several minor products like heptene, octanal, octanol and octane were also observed. When the catalyst temperature decreased to 235°C, OA conversion, and CO$_2$ selectivity, decreased to 38% and 40%, respectively. When the catalyst temperature was returned to 260°C and decreased to 240°C, selectivity to n-heptane dropped to 92% due to higher octanal and octanol production.

When the feed gas changed to 100% H$_2$, Pd/C (E) exhibited DCN activity with significantly lower conversion (Fig. 6). Only CO was produced (Fig. 6b), and the yields of CO and n-heptane are equivalent. The initial OA conversion is 45% and selectivity of heptane is 90% compared with 100% under 10% H$_2$. When, after 6 h TOS, the feed gas was switched to 10% H$_2$, CO$_2$ selectivity increased to 62% and OA conversion increased to 75%. The increase in conversion was due primarily to a marked increase in CO$_2$ production (Fig. 6b). Catalyst deactivation was accompanied by decreasing CO$_2$ selectivity.

OA deoxygenation over Pd/C (E) was investigated at 300 °C using 8 μL/min injection rate, giving higher inlet OA concentration and WHSV (0.88 h$^{-1}$). Initially, under H$_2$ atmosphere (Fig. 7a), OA conversion and CO$_2$ selectivity were 80% and 35%, respectively. CO$_2$ selectivity was greater than zero even under H$_2$ at 300 °C. After switching to 10% H$_2$, higher conversion
(~100%) and CO₂ selectivity (~80%) were observed, but the catalyst deactivated faster than at 260 °C. Concomitantly, the CO₂ selectivity dropped rapidly from nearly 80% initially to 45% after 15 h TOS. The higher CO₂ selectivity under 10% H₂ resulted from a decrease in CO yield and an increase in CO₂ yield (Fig. 7b). Only the decrease in CO₂ production contributed to the conversion decline, as the CO yield actually increased initially with TOS before becoming relatively constant. The yield of CO+CO₂ is in excellent agreement with yield of C₇, indicating that the material balance closed and that CO and CO₂ come only from the production of n-heptane (>99%). Toward the end of 10% H₂ period, the yield of diheptyl ketone began to increase. Interestingly, after ~15 h TOS under 10% H₂, when the feed gas was switched back to 100% H₂, CO₂ production decreased markedly (CO₂ selectivity < 10%), but CO production remained approximately constant.

Given the dramatic effect of H₂ partial pressure on catalytic activity and CO₂ selectivity, OA deoxygenation over Pd/C (E) was tested under 5% to 100% H₂ with 0.88 h⁻¹ WHSV and 100 sccm total gas flow rate. In Fig. 8, OA conversion and CO₂ selectivity decrease with increasing H₂ partial pressure. Under lower H₂ pressure (5% - 10%), high OA conversion with 70% CO₂ yield give evidence for a decarboxylation pathway. In contrast, OA conversion and CO₂ selectivity drop dramatically after the H₂ partial pressure is 0.5 atm or higher. With CO₂ yield decrease, CO yield starts to increase slowly. As shown in Fig 8(b), C₇ species yield has 1:1 relationship with yield of CO + CO₂, indicating that all the CO and CO₂ come from the formation of C₇ species via DCN and DCX. We infer that DCX is favored at low coverage of adsorbed hydrogen. A high partial pressure of H₂ inhibits the DCX pathway, and essentially only the DCN pathway is observed under 100% H₂.
Different WHSVs were obtained by adjusting the OA injection rate while keeping the OA injection /total gas flow rate ratio in the same time to hold the OA mole fraction constant. In this experiment, 4, 8, 12, 16 μL/min OA injection rates were used in 100, 200, 300, and 400 sccm total gas flowrate to get different WHSV value under 10% H₂ at 260 °C. As illustrated in Fig. 9a when OA conversion is plotted against 1/WHSV a non-linear relationship is observed indicating that this reaction is not zero order. Both OA conversion and CO₂ selectivity increase with reciprocal space velocity (space time). Plotting ln(1-X) versus 1/WHSV gives a highly correlated linear fit, as shown in Fig. 9b. Based on the excellent linear fit, the reaction appears to be first order in OA concentration under these conditions. Using the OA concentration in the feed to determine the zero-conversion rate, the turnover frequency (TOF) for OA deoxygenation is 0.026 s⁻¹ at 260°C.

3.4 OA Deoxygenation over 5 wt.% Pd/C (AA)

OA deoxygenation over Pd/C (AA) was investigated at 260°C using an OA injection rate of 4 μL/min. Under H₂ initially, OA conversion was ~85% and CO₂ selectivity was 0% (Fig. 10a). In contrast to the behavior of Pd/C (E), decreasing the H₂ partial pressure to 10% resulted in no significant change in OA conversion; however, the CO₂ selectivity did increase to ~55%. The higher CO₂ selectivity under 10% H₂ resulted from a decrease in CO yield and an increase in CO₂ yield (Fig. 10b). During 10% H₂ period, the catalyst began to deactivate rapidly with CO₂ selectivity decreasing at the same time. The loss in activity with TOS was primarily due to a decrease in CO₂ production. The catalyst appeared to stabilize after about 20 h TOS at 40% conversion and ~32% CO₂ selectivity. OA conversion actually decreased slightly when the feed gas was switched back to 100% H₂, as the loss of CO₂ production was not offset by
an equal increase in CO production. Also, octanal, octanol and octane (among minor products) had significant increase at 100% H₂ causing only 95% selectivity of n-heptane compare with 99% under 10% H₂.

3.5 OA Deoxygenation over Pd/CB

In order to better understand the support effect, a 5 wt.% Pd catalyst on a nonporous carbon black (CB) support was prepared. Pd/CB was tested under 10% H₂ and 100% H₂ at 260°C with 4 μL/min OA injection rate and 100 sccm gas flow rate, and the results are shown in Fig. 11. CO was the only gaseous product detected, and the yield of CO was consistent with yield of n-heptane (Fig 11b), indicating that OA undergoes DCN over Pd/CB. With fresh catalyst, higher H₂ pressure increased initial conversion from 35% to 82%, but faster deactivation was observed. After the catalyst had been on stream for 10 h, changing H₂ partial pressure had little effect on OA conversion. Under 10% and 100% H₂, OA conversion appeared to be trending toward ~15% after 15 h TOS.

3.6 Characterization of Used Pd/C Catalysts

The used 5% Pd/C (E), Pd/C (A), Pd/CB catalysts were characterized by nitrogen porosimetry and CO chemisorption, and the results are given in Table 2. The BET surface areas of used Pd/C (E) and Pd/C (AA) are lower than the fresh catalysts primarily due to loss/occlusion of micropores. In contrast, the Pd/CB surface area did not change, since fresh Pd/CB did not have micropores. The Pd dispersions of the used catalysts are all ~8%, and the used catalysts have lower dispersions than the fresh catalysts.
3.7 Water Gas Shift Reaction

Pd/C (E), Pd/C (AA) and Pd/CB were tested for WGS activity at 260 and 300°C by feeding DI water, CO, H₂ (balance He). The feed stream contained 1.25% CO and 0, 10 or 100% H₂. Liquid DI water was injected at 1 μL/min initially, and then the flow rate was adjusted to achieve different H₂O to CO ratios. Interestingly, only Pd/C (E) exhibited WGS activity at either 260 °C or 300 °C under 10% H₂; Pd/C (AA) and Pd/CB had negligible WGS activity. The Pd/C (E) WGS reaction results are shown in Table 3. At 260 °C, 0.094 h⁻¹ WHSV and 1:1 H₂O to CO ratio, CO conversion decreased with H₂ partial pressure increase, indicating that H₂ partial pressure inhibits CO conversion to CO₂. Under 10% H₂ at 260°C, which corresponds to typical OA deoxygenation conditions, by changing H₂O:CO mole ratio from 1:1 to 4:1, the CO conversion was increased proportionally from 5.5% to 16.4%. At 300°C, 0.19 h⁻¹ WHSV and H₂O:CO ratio of 1, CO conversions were a slightly higher than at 260°C under various H₂ percentage. At 300°C under He, Pd/C (E) was tested under different H₂O:CO mole ratios, and CO conversion increased from 12% and 32% (Table 3). Based on the differential (less than 10%) CO conversion results, the WGS reaction TOFs for Pd/C (E) under 10% H₂ at 260 °C and 300 °C were calculated to be 6.16 x 10⁻⁴ s⁻¹ and 1.85 x 10⁻³ s⁻¹, respectively.

4. Discussion

4.1 Support effect

The 4 different catalysts that were tested for OA deoxygenation can be generally divided into three categories: Pd on silica, Pd on activated carbon and Pd on carbon black. Each of these supports has a different pore size distribution. The high surface area activated carbon supports are microporous. The moderate surface area silica support has high volume of
mesopores, and the low-surface-area CB is essentially non-porous. Only Pd on activated carbon catalysts (Pd/C (E) and Pd/C (AA) show both DCX and DCN activity; Pd/SiO$_2$ and Pd/CB only exhibit DCN activity. Even for 5% Pd supported on a similar activated carbon support, deoxygenation performance varies because of the different Pd particle size. Pd/C (AA) which has higher Pd dispersion but similar BET surface area and micropore volume is inferior to Pd/C E117 in every respect: activity, stability and CO$_2$ selectivity. Also, H$_2$ partial pressure has a more significant effect on Pd/C (E) than Pd/C (AA).

Commercial Pd/SiO$_2$ was the only catalyst that produced significant yields of octanal and heptane in DCN pathway. H$_2$ promotes the DCN pathway by speeding up both of the octanal formation and octanal conversion to either heptane or octanol and octane. Pd/CB also exhibited only DCN activity; however, selectivity to $n$-heptane was always $>90\%$, even under 10% H$_2$, which is not like Pd/SiO$_2$.

4.2 Temperature effect

The commercial Pd/SiO$_2$ catalyst was tested at 245 °C, 260 °C and 300 °C, and conversion and heptane selectivity increased with temperature. As shown in Scheme 1 of possible reaction pathways of OA deoxygenation, octanal is an intermediate product of the DCN pathway that is subject to the rate of hydrodeoxygenation (HDO) of OA and decarbonylation of octanal. The increasing OA conversion and heptane selectivity at 300 °C suggests higher temperature increases the rates of both of HDO of OA and decarbonylation of octanal.

Similar temperature effect experiment was run on Pd/C (E) at 240 °C, 260 °C and 300 °C and both OA conversion and CO$_2$ selectivity increased with increasing temperature. According to Arrhenius equation (Eq. 4),
Increasing temperature increased OA deoxygenation rate thus OA conversion enhanced. As to selectivity of DCX and DCN, the relationship between these two parallel reactions rate ratio \( r_1 \) and \( r_2 \) are DCX and DCN rate respectively) and temperature as below:

\[
\frac{r_1}{r_2} = \frac{k_1}{k_2} = \frac{A_1}{A_2} e^{(E_{a1} - E_{a2})/RT} \propto e^{(E_{a1} - E_{a2})/RT}
\]  

\( E_{a1} \) and \( E_{a2} \) are assigned for DCX and DCN activation energy respectively. When reaction temperature increase if \( E_{a1} \) is larger than \( E_{a2} \), \( \frac{r_1}{r_2} \) will be higher, otherwise, \( \frac{r_1}{r_2} \) will be lower. \( \text{CO}_2 \) selectivity increased with increasing temperature suggesting that the DCX activation energy is higher than DCN activation energy. Heyden, et al [18]. Also point out the same result from the DFT calculations of propionic acid deoxygenation on Pd (111). According to WGS reaction over Pd/C (E), WGS reaction plays a greater role at high temperature at 300 °C leading to higher \( \text{CO}_2 \) selectivity. And this increasing WGS activity could also account to the \( \text{CO}_2 \) selectivity rise along with higher DCX activation energy.

4.3 \( \text{H}_2 \) effect

In OA deoxygenation over Pd/C (E), the DCN pathway is dominant under He, and the accumulation of alkenyl and carboxyl groups on Pd surface may be the reason for the rapid deactivation. Although \( \text{H}_2 \) is not required by the reaction stoichiometry, it is essential for OA deoxygenation, consistent with Maier’s early work [15]. The small presence of adsorbed hydrogen favors hydrogenation of alkenyl groups and prevents rapid and irreversible catalyst deactivation. At high partial pressure of \( \text{H}_2 \), the DCX pathway is inhibited, especially under
100% H$_2$, when only the decarbonylation pathway observed. Lamb and Whitten’s work on the mechanism of butanoic acid decarboxylation on Pd (111) has indicated adsorbed H influences reaction barriers and reference energies by competing with O for Pd electrons [19]. Meanwhile, higher partial pressure of H$_2$ promotes the decarbonylation pathway, basically, by shutting down the DCX pathway showed in Fig 8(a). But the increase of DCN activity cannot compensate the lost DCX activity, so OA conversion declines with H$_2$ percentage increases as well. For Pd/C (E) and Pd/C (AA) which both have DCX and DCN activity, when 100% H$_2$ was changed to 10% within the first 1-2 h TOS, there is a significant drop of CO signal, but after the catalyst has deactivated, 100% H$_2$ only has little effect on CO production. Moreover, under 100% H$_2$, selectivity of heptane was slightly lower under 10% H$_2$. Octanal, octanol, octane are minor products over Pd/C that were enhanced under 100% H$_2$. These results are consistent with Murzin’s recent conclusion that DCN via an aldehyde intermediate is favored over Pd/C under a hydrogen-rich atmosphere [17]. For Pd/CB which has only decarbonylation activity, there is a significant difference between reactions starting with 10% H$_2$ and 100% H$_2$. Although the OA initial conversion under 100% is higher than 10%, both catalysts deactivated to same level irrespective of initial H$_2$ partial pressure. For Pd/SiO$_2$, H$_2$ has a large promotional effect on DCN by speeding up octanal conversion to either heptane or octanol/octane and saturating double bond heptene. We infer that OA deoxygenation pathway is sensitive to H$_2$ partial pressure, and presence of H$_2$ changes deoxygenation mechanism.

4.4 Reaction pathways

There is an ongoing debate as to whether the water gas shift (WGS) reaction contributes to the DCX pathway. The DCN reaction can be combined with the WGS reaction and alkene
hydrogenation to give the DCX pathway. In OA deoxygenation experiment, Pd/C (E) had highest 65% CO$_2$ selectivity followed by 40% in Pd/C (A) and 0% in Pd/CB. According to our WGS test on these 3 catalysts, only Pd/C (E) was active at 260°C under 10% H$_2$. And the TOF of WGS is only 6.16e-04 s$^{-1}$ compare with 2.56e-02 s$^{-1}$ TOF of OA deoxygenation. Our results indicate that the WGS contributes very little to the DCX pathway over Pd/C (E) at 260°C and does not contribute at all to OA DCX over Pd/C (A). However, at 300°C, the WGS reaction does appear to contribute to higher CO$_2$ selectivity over Pd/C (E). DCX and DCN are independent parallel pathways that are sensitive to the catalyst support, Pd particle size, and reaction conditions (temperature, H$_2$ partial pressure).

Scheme 1 shows possible reaction pathways for OA deoxygenation. In addition to the known DCX and DCN pathways, there is an alternative pathway that combines hydrodeoxygenation (HDO) and decarbonylation (DCN) via an octanal intermediate, as shown in Eq 7 and 8

$$C_7H_{16}COOH + H_2 \rightarrow C_7H_{15}CHO + H_2O$$  (7)
$$C_7H_{15}CHO \rightarrow CO + C_7H_{16}$$  (8)
$$C_7H_{15}CHO + H_2\rightarrow C_8H_{17}OH \rightarrow C_8H_{18}$$  (9)

We note that, under this alternative pathway, heptene is not produced by DCN. For Pd/C (E) and Pd/C (AA) at lower H$_2$ partial pressure, octanal was difficult to detect; however, at higher H$_2$, OA underwent HDO to octanal. Octanal then decomposed through DCN producing CO and heptane. Some of the octanal was further hydrogenated to octanol and octane (Eq 9). Based on the results for OA deoxygenation under He, the Pd/C (E) catalyst deactivated very fast under DCN pathway when heptene was produced along with heptane. With absent of H$_2$,
HDO would be eliminated thus heptene can account for the production of direct DCN pathway. For Pd/SiO₂, heptene and octanal were both observed as intermediate products suggesting that initial C-C cleavage for direct DCN pathway and HDO for alternative DCN pathway were exist simultaneously.

5. Conclusion

We systematically investigated support, temperature, H₂ effects on vapor phase OA deoxygenation. Pd on activated carbon, silica and carbon support were tested to elucidate the support effect. Due to the different poresize distribution, 5% Pd/C (E) and Pd/C (AA) with microspore exhibits decarboxylation activity along with decarbonylation pathway. 5% Pd/SiO₂ and PdCB without microspore demonstrated decarbonylation activity only. Microporous support is the key factor for decarboxylation pathway. Under high reaction temperature, both of decarboxylation/decarbonlyation rates were promoted but more significant on decarboxylation. For H₂ effect, without H₂, catalyst was inactive and deactivated very fast which is totally different in liquid phase result. Small amount of H₂ boosts the decarboxylation pathway and large amount of H₂ inhibit decarboxylation pathway and promotes decarbonylation pathway especially under fresh catalyst. Octanal as second major product (except heptane) was first observed under Pd/SiO₂ and Pd/C with rich H₂ environment. In both case, decarbonylation is the dominate pathway, so octanal was introduced to be the intermediate product in an alternative pathway that combines hydrodeoxygenation (HDO) and decarbonylation (DCN). And the TOF of WGS over Pd/C (E) was calculated to be only 6.16e-04 s⁻¹ compare with 2.56e-02 s⁻¹ TOF of OA deoxygentaion. That indicates WGS has very little
contributes to the decarboxylation pathway on Pd/C (E). Decarboxylation is an independent pathway and selective to the catalyst support and particle size.
References


Table 1. Catalyst characterization results

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Dispersion&lt;sup&gt;a&lt;/sup&gt; (%)</th>
<th>Particle size&lt;sup&gt;b&lt;/sup&gt; (nm)</th>
<th>BET Surface Area&lt;sup&gt;c&lt;/sup&gt; (m²/g)</th>
<th>Micropore Volume&lt;sup&gt;c&lt;/sup&gt; (cm³/g)</th>
<th>Total pore Volume&lt;sup&gt;c&lt;/sup&gt; (cm³/g)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% Pd/C (E)</td>
<td>15.8</td>
<td>7.1</td>
<td>855</td>
<td>0.21</td>
<td>0.62</td>
<td>9.4</td>
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<tr>
<td>5% Pd/C (A)</td>
<td>31.5</td>
<td>3.5</td>
<td>820</td>
<td>0.17</td>
<td>0.68</td>
<td>5.3</td>
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<tr>
<td>5% Pd/CB</td>
<td>19.4</td>
<td>5.7</td>
<td>88</td>
<td>0.0061</td>
<td>0.28</td>
<td>7.1</td>
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<tr>
<td>5% Pd/ SiO₂</td>
<td>5.2</td>
<td>15</td>
<td>212</td>
<td>0.0062</td>
<td>0.83</td>
<td>6.8</td>
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</table>

<sup>a</sup>: dispersion measured by micrometrics ASAP 2020C, with stoichiometry factor 1:1.5
<sup>b</sup>: particle diameter estimated from dispersion
<sup>c</sup>: total pore volume of pores less than 1000 Å at p/p₀=0.
Table 2. Used catalyst characterization results

<table>
<thead>
<tr>
<th>Used Catalyst</th>
<th>Dispersion&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Particle size&lt;sup&gt;b&lt;/sup&gt; (nm)</th>
<th>BET Surface Area (m&lt;sup&gt;2&lt;/sup&gt;/g)</th>
<th>Micropore Volume (cm&lt;sup&gt;3&lt;/sup&gt;/g)</th>
<th>Total pore Volume&lt;sup&gt;c&lt;/sup&gt; (cm&lt;sup&gt;3&lt;/sup&gt;/g)</th>
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<td>5% Pd/C (E)</td>
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<td>15.0</td>
<td>675</td>
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<tr>
<td>5% Pd/C (A)</td>
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<td>0.67</td>
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<tr>
<td>5% Pd/CB</td>
<td>7.9</td>
<td>14.1</td>
<td>81</td>
<td>0.0044</td>
<td>0.28</td>
</tr>
</tbody>
</table>

a: dispersion measured by micrometrics autochem 2920 plus chemisorption, with stoichiometry factor 1:1.5
b: particle diameter estimated from dispersion
c: total pore volume of pores less than 1000 A at p/p<sub>0</sub>=0.97
Table 3. Pd/C (E) water gas shift reaction results

<table>
<thead>
<tr>
<th>Temperature</th>
<th>WHSV(CO)h⁻¹</th>
<th>H₂O/CO</th>
<th>He</th>
<th>10% H₂</th>
<th>H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>260°C</td>
<td>0.094</td>
<td>1</td>
<td>10.00%</td>
<td>4.00%</td>
<td>3.50%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>5.5%⁺</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>11.30%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>16.40%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>300°C</td>
<td>0.19</td>
<td>1</td>
<td>12.00%</td>
<td>7.50%</td>
<td>6.50%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>21.00%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>32.00%</td>
<td></td>
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</tr>
</tbody>
</table>

a: reaction start with 10% H₂
Figure 1. (a) TEM image of 5% Pd/C (E), (b) Pd partial size distribution of 5% Pd/C (E)
Figure 2. (a). Conversion and yield of heptane, heptene and octanal (b) Yield of CO and CO$_2$ in the reaction of 4 μL/min OA vapor deoxygenation over 5% Pd/SiO$_2$ under different hydrogen partial pressure in 100sccm at 260°C and atmosphere pressure.
Conversion
Yield Heptane
Yield Heptene
Yield Octanal
TOS (h)

(a)
Figure 3. (a) OA Conversion (b) Yield of heptane, octanal and heptene in the reaction of 4 μL/min OA vapor deoxygenation over 5% Pd/SiO$_2$ under 10% H$_2$ at 245°C, 260 °C and 300 °C in and atmosphere pressure.
Figure 4. (a) Yield of heptane, heptene and octanal (b) QMS data for CO and CO₂ mole fraction in the reaction of 4 μL/min OA vapor deoxygenation over 5% Pd/C (E) under He in 100sccm at 260°C and atmosphere pressure.
Figure 5. OA conversion and selectivity of heptane and CO$_2$ in the reaction of 4 µL/min OA vapor deoxygenation over 5% Pd/C (E) under 10% H$_2$ in 100sccm at 260°C, 240 °C and atmosphere pressure.
Figure 6. (a). Conversion and selectivity of n-heptane and CO₂ (b) Yield of CO and CO₂ in the reaction of 4 μL/min OA vapor deoxygenation over Pd/C (E) under different hydrogen partial pressure in 100sccm at 260°C and atmosphere pressure.
OA conversion
Sc7
Sco2
Conversion/Selectivity
TOS (h)
100% H2 10% H2

(a)
Figure 7. (a) Conversion and selectivity of n-heptane and CO$_2$ (b) Yield of CO and CO$_2$ in the reaction of 8 μL/min OA vapor deoxygenation over Pd/C (E) under different hydrogen partial pressure in 100 sccm at 300°C and atmosphere pressure.
Conversion

n-C$_7$H$_{16}$ selectivity

CO$_2$ selectivity

TOS(h)

H$_2$

10% H$_2$

H$_2$

Conversion

n-C$_7$H$_{16}$ selectivity

CO$_2$ selectivity

(a)
Yield vs. TOS (h) for different hydrogen concentrations.

- CO$_2$
- CO
- CO$_2$+CO

(b)
Figure 8. a) OA conversion and CO₂/CO yield as a function of H₂ partial pressure. (b) linear relationship between CO₂ selectivity and conversion in the reaction of 8 μL/min OA vapor deoxygenation over Pd/C (E) at 260°C and atmosphere pressure.
Figure 9. (a) OA conversion and CO\textsubscript{2} selectivity as a function of 1/WHSV (b) ln (1-X) vs. 1/WHSV
Figure 10. (a) Conversion and selectivity of n-heptane and CO₂ (b) Yield of CO and CO₂ in the reaction of 4μL/min OA vapor deoxygenation over Pd/C (A) under different hydrogen partial pressure in 100sccm at 300 °C and atmosphere pressure.
(a)
(b)
Figure 11. (a) Conversion and selectivity of n-heptane (b) Yield of CO and CO$_2$ in the reaction of 4uL/min OA vapor deoxygenation over Pd/CB  start with 10% H$_2$ and 100% H$_2$ separately in at 260°C and atmospheric pressure.
Conversion OA
n-C\textsubscript{7}H\textsubscript{16} selectivity
Conversion/Selectivity
TOS (h)
H\textsubscript{2}
10\% H\textsubscript{2}
10\% H\textsubscript{2}
H\textsubscript{2}

(a)
(b)
Scheme 1. Reaction possible pathways of OA deoxygenation

\[
\text{WGS: } \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2
\]
Catalytic Deoxygenation of Octanoic Acid over Silica-Supported Pd and PdAu Catalysts

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Keywords: palladium, gold, bimetallic, deoxygenation, catalyst deactivation
Abstract

Catalytic deoxygenation of octanoic acid (OA) to n-heptane was investigated over silica-supported Pd and PdAu catalysts at 260ºC and 1 atm using a fixed-bed micro-reactor with online gas chromatography. Particle size effects were investigated using Pd/SiO₂ catalysts prepared by two different methods: a 1.78 wt.% Pd/SiO₂ with an average Pd particle size of 7.5 nm and a broad size distribution prepared by incipient wetness, and a 0.6 wt.% Pd/SiO₂ catalyst containing 1.5-nm particles with a narrow size distribution prepared by ion exchange. The catalysts were characterized by CO chemisorption, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and high-resolution transmission electron microscopy (HRTEM). The larger supported nanoparticles exhibited well-defined surface facets, as evidenced by HRTEM, and adsorbed CO preferentially at 2-fold bridging sites, as evidenced by DRIFTS. The smaller supported nanoparticles exhibited strong linear and bridging ν_{CO} bands. The more highly dispersed Pd/SiO₂ catalyst had initial OA deoxygenation activity, but deactivated rapidly and irreversibly with time on stream (TOS). In contrast, the 1.78 wt.% Pd/SiO₂ catalyst deactivated less rapidly with TOS and could be regenerated by heating in H₂ to remove OA residues. The catalyst deactivation mechanism is inferred to be self-poisoning by OA and CO. Addition of Au to Pd/SiO₂ was found to improve catalyst stability without significantly reducing catalytic activity. PdAu/SiO₂ (1:1 atomic ratio) and PdAu/SiO₂ (1:1.5 atomic ratio) catalysts were prepared using a procedure previously reported to produce supported Pd-Au alloy nanoparticles. The geometric and electronic effects of alloying Pd with Au reduce the CO adsorption energy and mitigate self-poisoning by OA (and related species).
1. Introduction

First-generation biofuels (e.g. bioethanol, biodiesel) are widely known as substitutes for their fossil counterparts, gasoline and diesel. Due to some limitations of first-generation biofuels, e.g., nitrous oxide emissions [1], poor oxidative stability, lower energy density and incompatibility with engines and transportation fuel infrastructure [2,3], second-generation biofuels that can be manufactured from various types of biomass have been developed to produce current transportation fuels replacement. With the advent of algal oil technology, large quantities of fatty acids (FAs) can be produced using minimal farmland to provide biologically derived transportation fuels for the future [4]. Catalytic deoxygenation of FAs is the key enabling technology in the conversion of triglycerides (algae lipids) to hydrocarbon transportation fuels [5].

FA deoxygenation can be achieved by either decarboxylation or decarbonylation [6-8]. The stoichiometric equations displayed below are for octanoic acid (OA) deoxygenation:

$$\text{C}_7\text{H}_{15}\text{COOH} \rightarrow n\text{-C}_7\text{H}_{16} + \text{CO}_2$$  (Decarboxylation)

The products of decarboxylation are CO$_2$ and a linear alkane.

$$\text{C}_7\text{H}_{15}\text{COOH} \rightarrow \text{CO} + n\text{-C}_7\text{H}_{14} + \text{H}_2\text{O}$$  (Decarbonylation)

Decarbonylation yields CO, H$_2$O and an alkene. The decarboxylation pathway is preferred, because it eliminates the additional cost of H$_2$ for alkene hydrogenation and generation of CO, a noble metal catalyst poison.

Early work by Maier, et al. showed that Pd/SiO$_2$ was active for vapor-phase deoxygenation of carboxylic acids (including OA) in flowing H$_2$. In contrast, no reaction was observed when using an inert carrier gas (N$_2$). They inferred “the active catalytic site may not be Pd itself but
rather a Pd/H complex” [9] More recently, Murzin and coworkers have reported extensive investigations of liquid-phase FA deoxygenation for biofuels production.[6,10-14] Several transition metals like Ni, Ru, Pd, Ir, Os and Rh on silica, alumina and activated carbon were studied in a semi-batch liquid-phase stearic acid deoxygenation. Pd on activated carbon (Pd/C) was identified as most active and selective to n-heptadecane without stoichiometric consumption of H2. Boda, et al. studied OA deoxygenation over Pd/C at high pressure and suggested that, in the presence of H2, OA deoxygenation occurs via a formic acid intermediate, which then decomposes to CO and H2O[15]. In addition, alkyl chain length effect was studied on deoxygenation kinetics for C8-C18 fatty acids by Ford, et al [16]. As FA carbon number decreased, reaction time and H2 consumption increased and CO2 selectivity and initial decarboxylation rate decreased. The increase in initial decarboxylation rates for longer chain FAs was attributed to their greater propensities to adsorb on the activated carbon support.

Bimetallic catalysts have attracted great attention because of their enhanced catalytic stabilities, activities and selectivities, as compared with their single-metal constituents [17]. Among the various bimetallic catalysts, Pd-Au has been intensively investigated and employed as catalyst for many important applications such as vinyl acetate (VA) synthesis [18], low temperature CO oxidation [19], and formic acid decomposition [20], and aldehyde preparation from alcohol oxidation [21]. Enhancement of catalyst stability, activity and selectivity may be attributed to geometric (ensemble) and electronic (ligand) effects. Both types of effects have been used to describe the catalytic modification of Pd by Au [18].

In this work, OA deoxygenation was investigated using Pd/SiO2 catalysts prepared by incipient wetness and ion exchange methods and varying H2 partial pressure and reaction
temperature to elucidate the particle size effect on OA deoxygenation. Vapor-phase deoxygenation of OA over PdAu/SiO\textsubscript{2} alloy catalysts was also investigated. Alloying Pd with Au was found to improve catalyst stability and prevent catalyst deactivation by self-poisoning.

2. Experimental Methods

2.1 Materials

OA (98+%) was purchased from Sigma-Aldrich and used as received. Ultra-high-purity (99.999%) He and H\textsubscript{2} were purchased from National Welders. Pd(NO\textsubscript{3})\textsubscript{2}·xH\textsubscript{2}O and [Pd(NH\textsubscript{3})\textsubscript{4}][NO\textsubscript{3}]\textsubscript{2} were purchased from Strem Chemicals. The hydrophilic fumed silica was Aerosil 300 (300 m\textsuperscript{2}/g) provided by Evonik Degussa.

2.2 Catalyst preparation and characterization

Pd/SiO\textsubscript{2} catalysts were prepared by incipient wetness impregnation (IW) and ion exchange (IE) procedures. A Pd/SiO\textsubscript{2} (IW) catalyst were prepared by impregnation of the SiO\textsubscript{2} support with a Pd(NO\textsubscript{3})\textsubscript{2} aqueous solution of minimal volume to form a thick paste. An aqueous solution of Pd(NO\textsubscript{3})\textsubscript{2} dissolved in 19 mL of deionized (DI) water was added to 4g of silica. The resultant material was dried at 40 °C overnight then calcined at 300 °C in flowing O\textsubscript{2} for 2 h. The Pd/SiO\textsubscript{2} (IE) catalysts were prepared by adding a [Pd(NH\textsubscript{3})\textsubscript{4}][NO\textsubscript{3}]\textsubscript{2} solution slowly drop-by-drop into an SiO\textsubscript{2}-water slurry. The solid was recovered by filtration and washed 3 times by DI water. The resultant paste was dried at 40 °C overnight and calcined at 250 °C flowing O\textsubscript{2} for 2 h. The bimetallic catalyst PdAu/SiO\textsubscript{2} was prepared by co-adsorption of [Pd(NH\textsubscript{3})\textsubscript{4}][NO\textsubscript{3}]\textsubscript{2} and [Au(en)\textsubscript{2}]Cl\textsubscript{3}, (en=ethylenediamine) onto silica gel from a pH 9 slurry [23]. After filtration and washing with DI water, the resultant paste was dried at 100 °C in air overnight, resulting in a purplish-brown powder. The Pd and Au loadings of each catalyst were
determined by Galbraith Laboratories using inductively coupled plasma-optical emission spectrometry (ICP-OES).

Pd dispersion was measured by CO chemisorption using a Micromeritics 2020c instrument. After reduction at 300 °C for 2 h, the adsorbed H₂ was removed by 4 h evacuation. Two isotherms were recorded: initial and after evacuation at 35 °C for 30 min. Thereafter, the catalyst chemisorption was calculated based on difference between strong and weak adsorbed CO at 35°C. The CO to Pd surface atom stoichiometric relationship was 1:1.5. The particle diameters (d) were calculated from the dispersion using the equation below [22]

\[ d = \frac{1.12}{D} \]

where D is the dispersion.

Temperature-programmed reduction (TPR) and temperature-programmed hydride decomposition (TPHD) measurements were performed using a Micromeritics 2920 AutoChem II instrument. Each catalyst was heated in 5% H₂/Ar to 300°C at 5°C/min (TPR) and held at 300°C for 1 h before cooling to ~40°C in flowing gas. Subsequently, decomposition of the β-Pd hydride phase was observed during heating under flowing 5% H₂/He at 5°C/min.

Diffuse-reflectance infrared Fourier transform (DRIFT) spectra of adsorbed CO were measured using a Bruker Vertex 70 FTIR spectrometer equipped with a Harrick Praying Mantis diffuse-reflectance accessory and a high-temperature in situ DRIFTS cell. Samples were reduced in the cell under flowing H₂ at 300 °C for 30 min, purged with He, and then cooled to room temperature under flowing He. For each sample, 1-mL pulses of 5% CO/He were used to saturate the catalyst surface until no significant change in the DRIFT spectrum.
was observed. All spectra consist of 128 scans collected at 4 cm\(^{-1}\) resolution using a liquid N\(_2\)-cooled MCT detector.

Transmission electron microscopy (TEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) were used to determine particle size distributions and atomic scale structure of the supported nanoparticles, respectively. Bright-field TEM images of each catalyst were acquired on FEI Tecnai G\(^2\) Twin instrument with 0.3-nm resolution at accelerated voltage 200kV at Duke University. High resolution HAADF-STEM imaging of the 1.78 wt. % Pd/SiO\(_2\) (IW) catalyst was done using a JEOL at 200 kvlocated at NCSU. An FEI Titan STEM with energy-dispersive x-ray (EDX) analysis capability was used to characterize the elemental composition of the PdAu nanoparticles.

2.2 OA deoxygenation experiments

OA deoxygenation experiments were conducted in a 0.5-in. stainless steel tubular reactor using 0.5 g catalyst powder suspended between quartz wool plugs. Catalyst temperature was measured using a Type K thermocouple in direct contact with the bed. Gas flow rate and composition to the reactor were set by mass flow controllers (Brooks), and OA was fed via high-pressure syringe pump (ISCO Serial D) at 4 μL/min (typical flow rate). The standard in situ catalyst pretreatment procedure was heating at 300 °C for 1 h in flowing H\(_2\). Typically, the catalyst was brought on stream at 260°C in flowing 10%H\(_2\)/He (100 sccm) for the first 8-10 h; then, the H\(_2\) mole fraction in the feed gas was increased to 100%. Alternatively, the catalyst was brought on stream under flowing H\(_2\) (100 sccm), and subsequently, the feed gas was switched to 10% H\(_2\)/He.
2.3 Analytical Methods

The reactor effluent was analyzed using dual on-line gas chromatographs (GCs). A Shimadzu GC-2010 equipped with a flame ionization detector (FID) and an Econocap EC-1 capillary column was used to determine OA, n-heptane, octanal, and heptene concentrations in the reactor effluent. Periodic sampling was achieved by 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, then an increase to 240 °C at 40 °C/min. FID responses were calibrated using a series of different concentrations of OA, n-heptane, 1-heptene and octanal in suitable solvents. An SRI GC equipped with a thermal conductivity detector (TCD) and a Restek ShinCarbon ST 100 column was used for monitoring CO and CO₂ concentrations. The GC-TCD was operated isothermally at 100 °C. A standard calibration mixture containing 5% CO, 5% CO₂, 5% H₂ and 1% CH₄ standard calibration gas (National Welders) was used to calibrate the GC-TCD for CO, CO₂ and CH₄ response factors.

3. Results and Discussion

3.1 Characterization of Pd/SiO₂ and PdAu/SiO₂ Catalysts

ICP-OES and CO chemisorption results for the Pd/SiO₂ and PdAu/SiO₂ catalysts are given in Table 1. Average Pd nanoparticle size and surface Pd atoms per gram of catalyst were calculated based on the Pd loading and dispersion values. The Pd/SiO₂ catalysts prepared by incipient wetness had much lower Pd dispersions than those prepared by ion exchange (~100% dispersion). The chemisorption-derived particle sizes of the Pd/SiO₂ (IE) samples are ~1 nm, and those of the Pd/SiO₂ (IW) samples are 6-8 nm. The Pd dispersions of the bimetallic catalysts are similar and intermediate between those of the Pd/SiO₂ (IW) and Pd/SiO₂ (IE)
catalysts. The calculated particle sizes of the PdAu/SiO₂ catalysts are ~4 nm (assuming no surface segregation of Pd). Among these catalysts, 1% Pd/SiO₂ (IE) had the highest density of Pd surface atoms per gram, and PdAu/SiO₂ (1:1.5) the lowest.

Figure 1 shows TEM images of fresh 1.78% Pd/SiO₂ (IW), 0.6% Pd/SiO₂ (IE) and PdAu/SiO₂ (1:1) catalysts. The 1.78% Pd/SiO₂ (IW) catalyst (Fig. 1a) has an average particle size of 7.5 nm with a relatively wide particle-size distribution (Fig. 2a). The average particle size determined by TEM shows good agreement with that determined by CO chemisorption (Table 1). A dark-field HAADF-STEM image of a typical Pd nanoparticle (Fig 1b) shows that the nanoparticles exhibit well-defined, low-index facets. The 0.6% Pd/SiO₂ (IE) catalyst contains small ~ 1-2 nm Pd particles, as seen in the dark-field STEM image in Fig. 1c. The average particle size is 1.5 nm with a narrow size distribution (Fig 2b). The TEM and CO chemisorption results evidence that the different catalyst preparation methods result in different Pd particle sizes. The isoelectric point of the SiO₂ support is approximately 2 and the pH of [Pd(NH₃)₄][NO₃]₂ is 10, meaning the surface is negatively charged and has a large attraction to Pd⁺. Pd particles prepared by IE are uniform and well-dispersed on the silica support. However, during incipient wetness impregnation the Pd solution is drawn into pores via capillary action, so the particles are larger and less uniform than IE prepared catalyst.

The alloy nanoparticles in the PdAu/SiO₂ (1:1) catalyst (Fig. 1d) have a 5-nm average diameter with relatively broad size distribution. The average particle size from TEM is ~25% larger than that from chemisorption (Table 1), consistent with Pd surface segregation (at least in the presence of adsorbed CO). The EDX maps (Fig. 3) of a randomly selected nanoparticle
from the PdAu/SiO$_2$ catalyst confirm the alloy structure, and there does appear to be more Pd than Au at the nanoparticle surface (based on the larger diameter in the Pd pixel map).

DRIFT spectra (Fig. 4) of CO adsorbed on the Pd/SiO$_2$ and PdAu/SiO$_2$ catalysts contain CO-stretching bands in the 2000-2100 and 1800-2000 cm$^{-1}$ regions, corresponding to linear (atop) and bridging (multi-coordinated) CO species, respectively [24]. For the Pd/SiO$_2$ (IW) catalysts which contains larger particles, a strong sharp bridging CO peak is observed at 1990 cm$^{-1}$ with a small linear CO peak at ~2090 cm$^{-1}$. The smaller particles exhibit more linear CO than bridging CO, in agreement with previous research [25]. Also, the ratio of Pd(100) to Pd(111) facets decreases with decreasing particle size [26], and the bridging CO band is shifted to the lower frequency (1930 cm$^{-1}$) on smaller particles due to the low index planes, such as a Pd(111) surface [27]. This information combined with HAADF-STEM images of 1.79% Pd/SiO$_2$ (IW) indicates that <100> facets are predominant on these supported particles. PdAu/SiO$_2$ exhibits two main CO peaks at 2070 and 1960 cm$^{-1}$ that are similar to those for Pd/SiO$_2$ (IE); however, these two peaks are smaller due to the lower concentration of Pd atoms on the particle surface. Moreover, there is a 30 cm$^{-1}$ red shift of the linear peak and a ~30 cm$^{-1}$ blue shift of the bridging CO peak. The bridging-to-linear peak ratio is greater >1. A shoulder peak near 2105 cm$^{-1}$ on Pd-Au/SiO$_2$ (1:1.5) is assigned to CO linearly adsorbed on Au atoms. In the case of bimetallic surface, not only did the intensity of both linear and bridged CO bonds decrease, but the FTIR peaks also shifted by varying degrees when compared with Pd/SiO$_2$ (IW) (2080 cm$^{-1}$ for linear and 1970 cm$^{-1}$ for bridged CO). This could be the result of electronic interaction between Pd and Au [28].
Because CO is a product of the OA decarbonylation pathway, incomplete CO desorption at reaction temperature may lead to catalyst poisoning. Thus, thermal desorption experiments were conducted in the DRIFTS cell after CO chemisorption at 25°C. Each catalyst was reduced at 300 °C for 1 h under flowing H₂, cooled to 25°C, and then saturated by pulsing CO into a flowing He stream. Subsequently, the temperature was increased from 25 to 260 °C (OA reaction temperature) in 50°C increments under flowing He. DRIFT spectra were recorded at 25°C to avoid thermal artifacts. As illustrated in Fig. 5a for the 0.6 wt.% Pd/SiO₂ catalyst, as temperature increased and CO coverage decreased, atop (linear) CO was removed faster and more completely than bridging CO due to the low coordination of linear bonding. Concomitant with CO desorption (reducing surface coverage), the atop and bridging peaks shift to lower wavenumbers due to reduction in dipolar coupling between adjacent adsorbed CO molecules [29]. Qualitatively, similar thermal desorption behavior was observed for the 1.78 wt.% Pd/SiO₂ catalyst, as evidenced by the DRIFT spectra in Figure 5b. For both monometallic catalysts, a significant fraction of the bridging CO species remain after thermal desorption at 260°C in flowing He. The thermal desorption behavior of the PdAu/SiO₂ catalysts (Fig. 6a-b) is different in several aspects. During CO desorption, the atop and bridging CO peak positions do not shift substantially until all (or nearly all, in the case of bridging CO) CO has desorbed from the catalyst. This suggests that alloying creates Pd surface sites that are more isolated and, consequently, not as affected by dipolar coupling. The surface coverage by bridging CO after thermal desorption at 260°C appears to be less than for the monometallic samples. We infer that the alloy PdAu structure weakens the interaction between CO and surface Pd atoms, allowing CO to be removed easier than from Pd/SiO₂ catalysts.
Temperature-programmed hydride decomposition (TPHD) can be valuable in assessing the degree of alloying in Pd-containing bimetallic catalysts [30]. For relatively large Pd particles saturated with hydrogen, a β-Pd hydride decomposition peak will be observed at ~55°C when the temperature is ramped linearly in flowing 5% H₂. For a well-alloyed sample, the β-Pd hydride peak will be absent due to the effects of alloying on bulk electronic structure. For small Pd nanoparticles (~ 1 nm in size), the high surface-to-volume results in a lower H/Pd ratio and a lower decomposition temperature. [31,32]. TPHD measurements were made on 3 catalysts: 1.78% Pd/SiO₂ (IW), 0.6% Pd/SiO₂ (IE) and Pd-Au/SiO₂. As shown in Figure 7, 1.78% Pd/SiO₂ (IW) has the largest peak at 55 °C, which was calculated to contain 0.65 mole H atoms per mole of Pd atoms. This number agrees well with the H/Pd ratio for bulk β-Pd hydride [33]. 0.6% Pd/SiO₂ (IE) had much smaller β-hydride peak with 0.16 mole H per mole Pd consistent with its 1-2 nm Pd particle size. The TPHD spectrum of PdAu/SiO₂ (1:1) shows no β-Pd hydride peak, suggesting this bimetallic catalyst is well alloyed.

3.2 OA deoxygenation over Pd/SiO₂ (IW)

A 3.88 wt.% Pd/SiO₂ (IW) catalyst was tested for OA deoxygenation under 10% and 100% H₂ at 260 °C, and catalyst performance with TOS is shown in Fig. 8. Although some CO₂ was produced initially, OA deoxygenation over this catalyst appears to proceed primarily via the decarbonylation pathway. A steady-state OA conversion under 10% H₂ of ~75% was achieved after ~10 h TOS. After 12 h TOS, H₂ partial pressure was increased to 1 atm resulting in a small increase in OA conversion. The CO yield agrees closely with the yield of n-heptane, suggesting OA decarbonylation is followed by rapid hydrogenation of 1-heptene. The effect of initial H₂ partial pressure was tested using a fresh 1.78 wt.% Pd/SiO₂ (IW) catalyst as shown
in Fig 9. Under equivalent reaction conditions (10% H₂, 260°C), the steady state conversion of 1.78% Pd/SiO₂ (IW) was ~40% compared with ~75% for the 3.88% Pd/SiO₂ (IW) catalyst consistent with its lower Pd loading. Like 3.88% Pd/SiO₂, 1.78% Pd/SiO₂ demonstrated relatively stable activity with TOS under 10% H₂. By changing initial H₂ partial pressure from 10% to 100%, the initial OA conversion increased from 55 to ~100%; however, the catalyst deactivation rate also increased, as shown in Fig 9. After 10 h TOS, the H₂ partial pressure was decreased to 10%, and OA conversion dropped to about the same level (actually, slightly lower) than observed for the catalyst that was brought on stream under 10% H₂. In contrast, for a fresh catalyst that had been run under 10% H₂ for 15 h TOS and achieved a steady-state OA conversion of 40%, increasing the H₂ partial pressure had little effect on OA conversion. It seems likely, given the current results showing that Pd/SiO₂ (IW) catalysts exhibit relatively stable activity with low deactivation and high H₂ partial pressure promotes decarbonylation pathway on fresh catalyst, that the fast deactivation observed under 100% H₂ is probably caused by an increased decarbonylation rate. Because CO cannot desorb completely at reaction temperature, the catalyst is poisoned rapidly.

3.2 OA deoxygenation over Pd/SiO₂ (IE) and PdAu/SiO₂

The experimental results for OA deoxygenation over 1.0 wt.% Pd/SiO₂ (IE) are shown in Fig. 10. The catalyst exhibited initial decarboxylation activity (as measured by CO₂ yield) under 10% H₂; however, this initial activity quickly decayed to near zero after 4 h TOS. Good agreement is observed between the n-heptane yield (Fig. 10a) and the CO + CO₂ yield (Fig. 10b) demonstrating closure of the material balance. Interestingly, decarbonylation activity (as measured by CO yield) did not decline significantly with TOS; therefore, we infer that the OA
conversion decrease was mainly from a decrease in decarboxylation activity. After 4 h TOS stream, the catalyst approached a steady-state conversion of 30% with nearly 100% n-heptane selectivity. At this point, the H₂ partial pressure was increased to 100%, and there was no change in OA conversion or CO₂ selectivity.

OA deoxygenation results are shown in Fig. 11 for the 0.6 wt.% Pd/SiO₂ and PdAu/SiO₂ (1:1.5) catalysts; these catalysts have similar Pd loadings but very different Pd dispersions (Table 1). The 0.6% Pd/SiO₂ catalyst gave an initial OA conversion of 45%, followed by fast deactivation to a steady-state conversion of 10-15%. The PdAu/SiO₂ catalyst had a similar initial conversion but exhibited negligible deactivation with TOS. The Pd surface atom density for 0.6% Pd/SiO₂ was 64 μmol/g and only 11 μmol/g for PdAu/SiO₂ (1:1.5). Due to the higher density of surface active sites, it was expected that 0.6% Pd/SiO₂ would have higher activity than PdAu/SiO₂; however, that was not observed. After each catalyst had reached the steady state (~ 7 h TOS), the H₂ partial pressure was increased, and, as before, there was no change in performance. During the deactivation of the 0.6% Pd/SiO₂ catalyst, there were some minor products formed, including diheptylketone, which caused a slight decline in the selectivity of the reaction to n-heptane. At lower conversions, the ketone yield is enhanced due to relatively high concentration of OA. In contrast, the PdAu/SiO₂ (1:1.5) catalyst maintained ~45% conversion for 8 h with very high selectivity to n-heptane. The PdAu/SiO₂ (1:1) catalyst performed this way as well. Yields of CO and CO₂ with TOS are shown in Figure 10(b). As with the 1% Pd/SiO₂ catalyst, the 0.6 wt.% Pd/SiO₂ catalyst exhibited initial decarboxylation activity. In contrast, the PdAu/SiO₂ catalyst did not show any decarboxylation activity; CO was the only gaseous product.
All the catalysts were tested for OA deoxygenation at 260°C and 1 atm under flowing 10% H₂, and the steady-state OA conversions and CO chemisorption results for selected used catalysts given in Table 2. OA conversion was approximately proportional to Pd loading for catalysts prepared using the same method. The 3.88% Pd/SiO₂ (IW) and 0.6% Pd/SiO₂ (IE) catalysts had similar initial Pd surface atom densities; however, 0.6% Pd/SiO₂ (IE) exhibited only a third of the conversion because of its rapid initial deactivation with TOS. The 1.78% Pd/SiO₂ and PdAu/SiO₂ catalysts gave similar OA conversion, but the PdAu/SiO₂ catalysts have much lower Pd loadings (and surface atom densities). Alloying Pd with Au, improved catalyst stability. Since OA deoxygenation occurred via the decarbonylation pathway, producing CO, incomplete CO desorption at reaction temperature may be one reason for Pd/SiO₂ catalyst deactivation. At 260 °C the order of remaining CO bridged coverage was determined as follows: 0.6% PdSiO₂ (IE) >1.78% PdSiO₂ (IW) > Pd-Au/SiO₂ (1:1) > Pd-Au/SiO₂ (1:1.5). This order correlates well with catalyst deactivation behavior. Pd-Au/SiO₂ had the lowest CO coverage (around 10-15%) at 260 °C. Only 1.78% Pd/SiO₂ and Pd-Au/SiO₂ were run under 100% H₂ to demonstrate the H₂ effect on fresh catalyst. The increased H₂ partial pressure increased decarbonylation over 1.78% Pd/SiO₂ and deactivation. There was no effect on Pd-Au/SiO₂. The turn over frequency has been tested for 1.78% Pd/SiO₂ and PdAu/SiO₂ (1:1.5) catalyst in table (2). Interestingly, they have similar TOFs, and alloy sample has a little bit higher activity, which suggest alloying Au with Pd didn’t change the reaction mechanism just help to eliminate the catalyst deactivation due to the weak adsorption of OA.
3.3 Characterization of used catalysts

DRIFT spectra of the fresh and used catalysts are shown in Fig 12. All the used catalysts display peaks around 2900 cm\(^{-1}\) and 1700 cm\(^{-1}\), which are assigned to sp\(^3\) C-H and C=O bond stretching frequencies, respectively. These IR absorption frequencies of organic functional groups evidence FA residues deposited on the catalyst surface. The observed peaks are consistent with IR spectrum of OA [34]. Subsequently, the used catalysts were treated in flowing H\(_2\) at 300 °C for 1 h and then purged with He. As shown in Fig. 12, adsorbed OA was removed from the 1.78% Pd/SiO\(_2\) (IW) and PdAu/SiO\(_2\) (1:1.5) catalysts, but remained on the 0.6% Pd/SiO\(_2\) (IE) catalyst. Analogously, DRIFT spectra of each used and recovered catalyst were taken after pulse CO adsorption (Fig 13). Because of OA residues, CO adsorption amount on used and recovered 0.6% Pd/SiO\(_2\) was much smaller than on the fresh catalyst, but for the 1.78% Pd/SiO\(_2\) (IW) catalyst CO adsorption amount was essentially unchanged (Table 2), consistent with the DRIFT spectra in Fig. 13a and 13b. DRIFTS of the PdAu/SiO\(_2\) (1:1.5) catalyst (Fig. 13c) indicate negligible loss of CO adsorption sites after catalysis. The DRIFTS analysis suggests that OA was adsorbed more strongly on the smaller Pd nanoparticles than larger nanoparticles, and the “atomic like” surface structure of Pd in the alloy PdAu/SiO\(_2\) catalyst caused a weak binding of OA [17].

Consistent with the DRIFTS spectra, the Pd dispersion of the used 1.78 wt.% Pd/SiO\(_2\) after post-reaction treatment in H\(_2\) at 300°C is equivalent to that of the fresh catalyst (Table 1). In contrast, chemisorption measurements on the used 1.0 and 0.6 wt.% Pd/SiO\(_2\) catalysts (after an equivalent post-reaction treatments) indicate a ~70-80% decrease in Pd dispersion. TEM images of the 0.6 wt. % Pd/SiO\(_2\) catalyst indicate no particle sintering under reaction
conditions, leading to the inference that adsorbed OA was the key reason for a loss of Pd dispersion and catalytic activity.

4. Conclusions

By screening Pd/SiO$_2$(IW), Pd/SiO$_2$ (IE), and PdAu/SiO$_2$ catalysts at 260 ºC under 10% H$_2$, it was found that Pd/SiO$_2$ catalyst was selective for decarbonylation pathway during OA deoxygenation, and that catalyst deactivation is related to Pd particle size. The ion exchange preparation method produced a highly dispersed Pd catalyst with small particle size and narrow size distribution. Small Pd particles exhibited strong linear and bridging $v_{CO}$ bands. This highly dispersed catalyst deactivated rapidly and irreversibly due CO and strongly adsorbed OA. STEM images of used catalyst showed negligible change in particle size, ruling out sintering as a key reason of deactivation [35]. Ion exchange catalysts had initial decarboxylation, and the decline of decarboxylation activity contribute to the catalyst deactivation showed decarboxylation occurs over different catalytic sites than decarbonylation which is consistence with Jeremy’s results (energy fuel).

Incipient wetness impregnation produced large Pd particles with an average size around 7.5 nm and a broad size distribution. The larger supported nanoparticles exhibited well-defined surface facets Pd (100), as evidenced by HRTEM, and adsorbed CO preferentially at 2-fold bridging sites, as evidenced by DRIFTS. The 1.78 wt.% Pd/SiO$_2$ catalyst deactivated less rapidly with time-on-stream and could be regenerated by heating in H$_2$ via removal of OA residues. Higher H$_2$ pressure increased the fresh catalyst decarbonylation initial rate, but due to abundant CO generated in the fast reaction rate, the catalyst deactivated faster than in 10% H$_2$. 
Addition of Au to Pd/SiO₂ was found to improve catalyst stability without significantly reducing catalytic activity. EDX-TEM and TPHD determined the Pd-Au alloy structure, and DRIFTS showed that the Pd-Au particles had both linear and bridging CO bond with little intensity. The geometric and electronic effects of alloying Au on Pd induced weak interaction between CO and OA and isolated Pd atoms, causing no deactivation at all. Pd-Au/SiO₂ showed no sensitivity to increases in H₂ partial pressure.
References


34. NIST Chemistry web book (http://webbook.nist.gov/chemistry/)

Table 1: Catalysts CO chemisorption results

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Dispersion (1:1.5) Fresh</th>
<th>Pd Particle size (nm)</th>
<th>Surface Pd atoms (μmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.88% Pd/SiO$_2$(IW)</td>
<td>17.7%</td>
<td>6.3</td>
<td>65</td>
</tr>
<tr>
<td>1.78% Pd/SiO$_2$(IW)</td>
<td>13.8%</td>
<td>8.1</td>
<td>23</td>
</tr>
<tr>
<td>0.6% Pd/SiO$_2$(IE)</td>
<td>122%</td>
<td>0.9</td>
<td>56</td>
</tr>
<tr>
<td>1% Pd/SiO$_2$(IE)</td>
<td>94%</td>
<td>1.2</td>
<td>90</td>
</tr>
<tr>
<td>0.44%Pd 0.91%Au/SiO$_2$(1)</td>
<td>28.7%</td>
<td>4</td>
<td>13</td>
</tr>
<tr>
<td>0.42%Pd 1.2%Au/SiO$_2$(1.5)</td>
<td>26.4%</td>
<td>4.2</td>
<td>11</td>
</tr>
</tbody>
</table>
Table 2: Summary of Catalysts OA Deoxygenation Activity

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Dispersion (1:1.5) Used</th>
<th>Conversiona (Steady state) %</th>
<th>TOF (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.88% Pd/SiO₂(IW)</td>
<td>-</td>
<td>71</td>
<td>-</td>
</tr>
<tr>
<td>1.78% Pd/SiO₂(IW)</td>
<td>13.1%</td>
<td>40</td>
<td>0.044</td>
</tr>
<tr>
<td>0.6% Pd/SiO₂(IE)</td>
<td>25%</td>
<td>22</td>
<td>-</td>
</tr>
<tr>
<td>1% Pd/SiO₂(IE)</td>
<td>33%</td>
<td>32</td>
<td>-</td>
</tr>
<tr>
<td>0.44%Pd 0.91%Au/SiO₂(1)</td>
<td>-</td>
<td>39</td>
<td>0.047ᵇ</td>
</tr>
<tr>
<td>0.42%Pd 1.2%Au/SiO₂(1.5)</td>
<td>-</td>
<td>43</td>
<td>-</td>
</tr>
</tbody>
</table>

a: reaction conditions: 260 °C, 1 atm, 10% H₂, 0.44 h⁻¹ WHSV
b: 260 °C, 1 atm, 10% H₂, 2.75 h⁻¹ WHSV (<10% conversion)
Figure 1. TEM images of (a, b) 1.78% Pd/SiO$_2$ (IW), (c) 0.6% Pd/SiO$_2$ (IE) and (d) PdAu/SiO$_2$(1:1)
Figure 2. Particle size distribution of (a) 1.78% Pd/SiO$_2$ (IW) and (b) 0.6% Pd/SiO$_2$ (IE) and (c) PdAu/SiO$_2$ (1:1).
dp=5nm
Figure 3. STEM-EDX of a PdAu alloy nanoparticle: (a) Pd-Au composite image, (b) Au image, and (c) Pd image.
Figure 4. DRIFTS of adsorbed CO on (a) 1.78% and 3.88Pd/SiO$_2$ (IW); (b) 0.6% and 1% Pd/SiO$_2$ (IE); (c) PdAu(1:1)/SiO$_2$ and PdAu(1:1.5)/SiO$_2$
(a) 

K-M Units
Wavenumbers (cm$^{-1}$)

(b) 

K-M Units
Wavenumbers (cm$^{-1}$)
Figure 5. DRIFT spectra of adsorbed CO on (a) 0.6% Pd/SiO₂ and (b) 1.78% Pd/SiO₂ catalysts. Thermal desorption temperatures (in flowing He) indicated in the legends.
Figure 6. DRIFT spectra of adsorbed CO on (a) PdAu/SiO₂ (1:1) and (b) PdAu/SiO₂ (1:1.5) catalysts. Thermal desorption temperatures (in flowing He) indicated in the legends.
Figure 7. TPHD spectra of 0.6% Pd\textsubscript{2}SiO\textsubscript{2} (IE), 1.78% Pd/SiO\textsubscript{2} (IW) and PdAu/SiO\textsubscript{2} (1:1) catalysts.
Figure 8. Yield n-C7 and yield CO in the reaction of 4uL/min OA vapor deoxygenation over 3.88% Pd/SiO2 (IW) under different hydrogen partial pressure in 100sccm at 260°C and atmosphere pressure.
Figure 9. a) Conversion b) Yield of CO and CO$_2$ in the reaction of 4uL/min OA vapor deoxygenation over 1.78% Pd/SiO$_2$ (IW) start with 10% H$_2$ and 100% H$_2$ separately at 260 °C and atmosphere pressure.
Figure 10. a) Conversion and Yield of n-heptane b) Yield of CO and CO$_2$ in the reaction of 4uL/min OA vapor deoxygenation over 1% Pd/SiO2 (IE) under different hydrogen partial pressure in 100sccm at 260 °C and atmosphere pressure.
Figure 11. (a) Conversion and Yield of n-heptane (b) Yield of CO and CO$_2$ in the reaction of 4uL/min OA vapor deoxygenation over 0.6% Pd/SiO$_2$ (IE) and PdAu/SiO$_2$ (1:1.5) under different hydrogen partial pressure in 100sccm at 260 °C and atmosphere pressure.
Figure 12. DRIFT spectra of (a) 0.6% Pd/SiO$_2$ (b) IW 1.78% Pd/SiO$_2$ and (c) PdAu/ SiO$_2$ catalyst comparing fresh, used and used catalyst after treatment in flowing H$_2$ at 300°C.
(a) 

(b)
Fresh
Used
Used and Reduced

K-M Units
Wavenumbers (cm⁻¹)
Figure 13. CO DRIFTS of used (a) 0.6% Pd/SiO₂ (b) IW 1.78% Pd/SiO₂ and (c) PdAu/SiO₂ (1:1) catalysts.
(a) [Graph showing wavenumbers (cm⁻¹) vs. K-M Units for Fresh, Used, and Used and Reduced samples.]

(b) [Graph showing wavenumbers (cm⁻¹) vs. K-M Units for Fresh, Used, and Used and Reduced samples.]
(c)
Palladium-Carbon Catalysts for Stearic Acid Deoxygenation to Heptadecane

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Keywords: biofuel, palladium, deoxygenation, support effect, Sodium promoted catalyst
Abstract

Liquid-phase catalytic deoxygenation of stearic acid (SA) to \( n \)-heptadecane (\( n \)-C\(_{17} \)) was investigated over a series of carbon-supported Pd catalysts at 300°C and 15 atm using a semi-batch reactor with on-line gas-phase monitoring. Commercial samples of 5% Pd/C (5) and lab-prepared 5% Pd/C (activated carbon) and 5% Pd/CB (carbon black) were screened under He and 5% H\(_2\) (balance He). The Pd/C catalysts were characterized by CO chemisorption, slurry pH, temperature-programmed desorption (TPD), temperature-programmed hydride decomposition (TPHD), and nitrogen porosimetry. Alkali carbonate salts on the surface were discovered to be the key factor in SA deoxygenation. Under He, all activated carbon (AC) supported catalysts were catalytically active for SA deoxygenation. Na- and K-rich catalysts Pd/C E117 and Pd/Calgon had the highest deoxygenation activity. In contrast, Pd/CB was inactive with only 8% SA conversion and high selectivity to decarbonylation. The catalyst activity under He was proven to be related to hydrogen spillover during \textit{in-situ} catalyst reduction. Under flowing 5% H\(_2\), 5 wt.% Pd catalysts on AC supports exhibited high conversion (90%) and high CO\(_2\) selectivity. Pd/Calgon had the lowest initial and maximum decarboxylation rate and showed some water gas shift (WGS) activity.
1. Introduction

First generation biofuels (bioethanol and biodiesel) are widely known as substitutes for their fossil counterparts, gasoline and diesel. Bioethanol, produced by fermentation of sugars derived from wheat, corn, sugarcane, etc., is the most common biofuel worldwide, particularly in Brazil. The history of bioethanol in Brazil dates from the 1970s and is related to sugarcane cultivation. From 2004 to 2011, Brazilian ethanol production increased from 3989 million gallons to 5573 million gallons. Global ethanol fuel production reached 23 billion gallons in 2010 and The United States is the world’s largest producer with a volume of 13.2 billion gallons. [1] Even though ethanol fuel has been successfully commercialized, it still has some disadvantages. First, ethanol in the US is mainly produced via corn, threatening food supplies and biodiversity. Low bioethanol yields from corn also translate to a very poor energy return on investment (EROI) between 0.75 and 1.4 [2,3]. Second, due to its low energy density and corrosive property, ethanol can be destructive to engine components and cannot be considered as a drop-in replacement for petroleum-based fuel. [4]

Biodiesel is a fatty acid methyl ester (FAME) derived from triglycerides (fats and oil) via transesterification with methanol can be used as a drop-in replacement for diesel fuel (B100) or be blended with diesel in concentrations up to 20%. However, biodiesel has many undesirable physical and chemical properties such as its high viscosity, high cloud point temperature, poor oxidation stability, and lower energy density. [5, 6]. These limitations spurred the development of second generation biofuels for fossil fuel replacement. Second generation biofuels are manufactured from various types of biomass. Algal oils technology produces high quantities of fatty acids (FAs) using minimal farmland to provide biologically
derived transportation fuels for the future [5]. Catalytic deoxygenation of free fatty acids (FFAs) is the key enabling technology in the conversion of triglycerides (algal lipids) to hydrocarbon transportation fuels [7-15]. FA deoxygenation can be achieved by either decarboxylation or decarbonylation. The equations displayed below are for OA [8].

\[ \text{C}_7\text{H}_{15}\text{COOH} \rightarrow \text{n-}\text{C}_7\text{H}_{16} + \text{CO}_2 \]  
\text{(Decarboxylation)}  \quad (1)

The products of decarboxylation are \( \text{CO}_2 \) and one carbon less linear alkane.

\[ \text{C}_7\text{H}_{15}\text{COOH} \rightarrow \text{CO} + \text{n-}\text{C}_7\text{H}_{14} + \text{H}_2\text{O} \]  
\text{(Decarboxylation)}  \quad (2)

Decarbonylation yields \( \text{CO}, \text{H}_2\text{O} \) and one carbon less alkene, which must be saturated by \( \text{H}_2 \). The decarboxylation pathway is preferred, because it eliminates the additional cost of hydrogen and generation of \( \text{CO} \), a noble metal catalyst poison.

Early work by Maier, et al. [16] showed that Pd/SiO\(_2\) was active for gas-phase deoxygenation of carboxylic acids in flowing \( \text{H}_2 \). In contrast, no reaction was observed when using an inert carrier gas (N\(_2\)). They inferred “the active catalytic site may not be Pd itself but rather a Pd/H complex”. More recently, Murzin’s group reported extensive investigations of liquid-phase stearic acid (SA) deoxygenation for biofuels production (Murzin group). Several transition metals like Ni, Ru, Pd, Ir, Os and Rh on silica, alumina and activated carbon were studied in a semi-batch liquid phase reaction and Pd on activated carbon (Pd/C) was identified as most active and selective to \( n\text{-C}_{17} \) without stoichiometric consumption of \( \text{H}_2 \) [8]. Murzin et al. also studied various 5 wt\% Pd/C catalysts for the deoxygenation of ethyl stearate. They examined catalyst acidity, type of feed, effect of solvent and gas atmosphere and found out the gas atmosphere and the acidity of catalysts were important factors for determine product
selectivity. Over most alkaline Pd/C catalyst under H₂ atmosphere gave the highest yields and initial deoxygenation rates, as well as the highest selectivity to n-heptadecane.[10] They proposed the reason for higher selectivity to n-heptadecane over alkaline catalysts was the capability of stearic acid to react further over such catalysts is stronger than acidic catalyst. The drawback in using an alkaline Pd/C catalysts was the substantial formation of aromatic side products. They also studied the effect of Pd dispersion on deoxygenation of palmitic and stearic acid mixture over 1 wt% Pd on Sibunit carbon catalysts in a semi-batch reactor [11]. They concluded that there is an optimum Pd dispersion by holding the weight and carbons support constant; however, the different metal dispersions catalysts were achieved by changing the pH of the palladium precursor solution. So along with Pd dispersion, acidity of catalysts also changed. According to the previous reference, alkaline Pd/C has higher catalytic activity on stearic acid and ethyl stearate deoxygenation. It is hard to rule out the effect of pH. Besides, their TEM mean particle size results do not agree well with their CO chemisorption measurements. Going by the TEM results, highest Pd dispersion catalyst had similar particle size with medium (optimum) Pd dispersion, making a concrete conclusion hard to draw. More recently, the effect of Na promotion on the elective hydrogenation of 4-siobutylacetophenone, 4-IBAP was investigated over a Pd/C catalyst by Cho et al. [17] The Na-promoted Pd/C resulted in a significantly improved yield for desired product, 1-(4-isobutylphenyl) ethanol (4-IBPE). They proposed the enhancement of Na-promoted PdC was related to the geometric and electronic effects of reactant in the microporous support.

In this work, liquid-phase deoxygenation of SA in dodecane at 300 ºC and 15 atm was employed to screen supported noble metal catalysts for decarboxylation of free fatty acids to
hydrocarbons. 5% commercial Pd on active carbon (Pd/AC) catalysts and lab prepared Pd/AC and Pd on carbon black (Pd/CB) were screened under He and 5% H$_2$. And all the catalysts have been characterized by CO chemisorption, TPD, TPHD, pH measurement and ICP-OES to reveal the key catalyst surface properties for SA deoxygenation like support effect (activated carbon VS. carbon black), pH effect and alkali metal promoters (Na, K, etc) on SA deoxygenation.

2. Experimental Methods

2.1 Materials

SA (95%) and dodecane (C$_{12}$, 99%+) were purchased from Sigma-Aldrich and used as received. Certified ultra-high-purity He and H$_2$ and zero grade air were obtained from National Welders. Commercial catalysts were obtained from various company. Commercial 5 wt. % Pd on activated carbon (Pd/AC) catalysts were provided by Evonik-Degussa (E117, E101, E199), Alfar-Aesar (AA38300) and BASF Strem Chemicals (EscaT 1971). The E199 and E101 catalysts had an eggshell Pd distribution where the Pd particles are primarily on or near the surface of the activated carbon support. The Pd in E117 has a uniform distribution over carbon support. For lab prepared catalysts, acetylene carbon black (~200 mesh powder) was obtained from Strem Chemicals, and activated carbon support was purchased from Calgon (OVC 4 x 8 type). 5 wt. % and 2 wt % Pd on carbon black and Pd on activated carbon catalysts (Pd/Calgon) were prepared by impregnation of carbon support with an aqueous solution of Pd(NO$_3$)$_2$ (Strem chemicals) using the incipient wetness technique. The resultant material was dried in air at 80 ºC overnight and then reduced $\text{ex situ}$ at 300 ºC in flowing H$_2$ for 1 h.
2.2 Catalyst characterization

The specific surface area and pore volume were obtained through \( \text{N}_2 \) porosimetry on a Micromeritics ASAP 2020C instrument. The carbon-supported catalysts were pretreated under vacuum at 300 °C for 8 h before \( \text{N}_2 \) physisorption measurements at 77 K. The Brunauer-Emmett-Teller (BET), Barrett-Joyner-Halenda (BJH) and t-plots methods were used to determine the surface area, mesopore volume, and micropore volume, respectively. Pd dispersion was measured by CO pulses and volumetric chemisorption using a Micromeritics ASAP 2020C. After reduction at 300 °C for 2 h, the absorbed \( \text{H}_2 \) was removed by 4 h evacuation. Thereafter, the catalyst chemisorption was performed at 35 °C for the CO volumetric measurement. The CO to Pd surface atom stoichiometric relationship was 1:1.5. pH of each catalysts were measured using pH meter after a slurry containing 0.3 g sample and 20 mL DI water was stirred for 1 h.

The amount of surface oxygen groups was analyzed by temperature-programed desorption (TPD). 0.4 g of catalyst were reduced at 300 °C for 1 h under flowing \( \text{H}_2 \), then cooled down to room temperature under flowing He. After that CO, \( \text{CO}_2 \) and \( \text{H}_2 \) desorption were monitored by quadrupole mass spectrometry (QMS) during a 5 °C/min temperature ramp from room temperature to 500 °C and 800 °C respectively. Temperature-programmed hydride decomposition (TPHD) was measured at low temperature on a Micromeritics 2920. Before the TPHD for each catalyst, temperature-programed reduction (TPR) was conducted up to 300 °C with 1 h soak time for the \( \text{H}_2 \) uptake. The \( \beta \)-hydride phase decomposition peaks were expected to be observed during the temperature ramping program with flowing 5% \( \text{H}_2/\text{He} \). The metal content was determined by ICP-OES.
2.3 SA deoxygenation experiments

Semi-batch SA deoxygenation experiments were conducted in a 50-mL stirred autoclave (Autoclave Engineers). Gas flow rate and purge gas composition were set by mass flow controllers (Brookes 5850E series). A 20-mL condenser was used to collect the reactor effluent. The reactor pressure was controlled by a manual back-pressure regulator (BPR, Tescom) located downstream of the condenser.

In a typical experiment, 22.5 g C\textsubscript{12} (solvent, 30 mL) and 336 mg of catalyst (dried overnight at 40 °C) were added to the reactor. The catalyst was suspended in the solvent using 240 rpm agitation rate. 60 mL/min He was used to remove air from reactor and condenser before reduction. After flowing 30 mL/min H\textsubscript{2} for 5 min, the pressure was increased to 2 atm. Catalysts were reduced \textit{in situ} at 200 °C using a 5 °C/min temperature ramp rate followed by a 1 h soak. The reactor was cooled to room temperature under H\textsubscript{2} before switching back to 60 mL/min He. The reactor was removed under He, and approximately 5.6 mmol SA were added to the reactor manually. The reactor was sealed and purge with 60 mL/min He until air had been removed. (Overnight for He experiments). The reactor pressure was then increased to 15 atm. The agitation rate was increased to 1000 rpm. After obtaining a baseline via QMS, the reactor was heated to 300 °C at a rate of 5 °C/min, follow by a soak at 300 °C for 4 h. After the reaction finished, the reactor was cooled to room temperature. Liquid products from the condenser and reactor were obtained and analyzed for composition via GC-FID.

2.4 Analytical Methods

The reactor gas effluent was analyzed on-line using a QMS (Pfeiffer Prismaplus) with a heated capillary inlet and Quadstar-32 bit software. The H\textsubscript{2} (2 m/z), He (4 m/z), CO (28 m/z),
and CO2 (44 m/z) signals were monitored once every minute. Certified mixtures containing 20% CO2 in He and 5% CO in He were used to calibrate CO and CO2 signals. The CO signals have been corrected for CO2 ionization to CO+ (28 m/z) by subtraction 10% of the CO2+ (44 m/z) intensity.

Reactor and condensate samples were analyzed using an HP5890 gas chromatograph (GC) equipped with a flame ionization detector (FID) and an Econocap EC-5 30 m x 0.32 mm x 1.0 um capillary column. Chromatograms were collected using and SRI model 333 peak simple chromatography data system. The GC oven temperature program was used: 5°C /min ramp from 80 to 300 °C, 1 min soak at 300 °C. 0.05 uL liquid samples were injected into column inlet with 50:1 split ratio. SA and n-C17 concentrations were determined using an n-decane standard.

2.5 Reactor Modeling- Initial Rates Calculation

In order to derive reaction kinetics from the on-line QMS data, it was necessary to relate the measured product partial pressure in the reactor effluent to the reaction rate. The CO2 mole balance below assumed that the stirred autoclave contents (liquid and gas phases) were well-mixed; therefore, the effluent composition reflected the instantaneous gas-phase composition in the reactor.

\[
\frac{Q}{RT} \left( P_{CO_2, in} - P_{CO_2, out} \right) + r_{CO_2} W = \frac{V_g}{RT} \left( \frac{dP_{CO_2}}{dt} \right)
\]

In the above equation, \( r_{CO_2} \) is the rate of CO2 generation, \( Q \) = purge rate, \( W \) = catalyst weight, \( V_g \) = volume of reactor head space, \( R \) is the gas constant, and \( T \) is the absolute temperature.

Since the CO2 partial pressure in the feed is negligible (\( P_{CO_2, in} \sim 0 \)), Eq. 1 simplifies to:
\[ r_{CO_2} = \frac{Q}{WRT} \left[ P_{CO_2,\text{out}} + \frac{V_g}{Q} \left( \frac{dP_{CO_2}}{dt} \right) \right] \]  

(2)

The CO\textsubscript{2} partial pressure is proportional to the 44 m/z signal. Before the reaction commences 
P_{CO_2,\text{out}} is approximately zero. And the initial rate is proportional to \( \frac{dP_{CO_2}}{dt} \). The material balance simplifies to the following equation for initial rates:

\[ r_{CO_2} = \frac{V_g}{WRT} \left( \frac{dP_{CO_2}}{dt} \right) \]  

(3)

\( \frac{dP_{CO_2}}{dt} \) was calculated by fitting the initial slope of a P\textsubscript{CO2} vs. t plot with a linear regression.

3. Results and Discussion

3.1 Commercial 5% Pd/C Catalysts

3.1.1 Catalyst Characterization

The 5 wt.% Pd/C catalysts and the E117 activated carbon (AC) support were characterized by N\textsubscript{2} porosimetry. The specific surface area, micropore volume and total pore volume of each sample are given in Table 1. All the Pd/C catalysts had BET surface areas between 750-850 m\textsuperscript{2}/g, and micropore volumes in the 0.17-0.21 cm\textsuperscript{3}/g range. The BET surface area and micropore volume of the Pd/C E117 catalyst are equivalent to those of the support material; the total pore volume of the catalyst is \( \sim \)15\% less than the support. Pd dispersions determined by pulse and volumetric CO chemisorption (assuming a 1.5 to 1 Pd surface atom to adsorbed CO stoichiometry) are given in Table 1. Pd/C E117 and Pd/C Escat had lower dispersions indicating average Pd particle sizes of \( \sim \)7 nm—too large to fit within the support micropores.
Compared with Pd/C E117 and Pd/C Escat, the other Pd/C catalysts had smaller particle sizes (<5 nm) based on their higher Pd dispersions. The H/Pd ratios from TPHD (also in Table 1) are consistent with the Pd dispersions of the catalysts. Larger Pd particles have greater bulk H₂ uptake (based on their smaller surface-volume ratios); therefore, Pd catalysts with lower dispersions have higher bulk H/Pd ratios.[18]

Additional properties of catalysts, such as slurry pH, Na, K content and total carbonate, bicarbonate, and carboxylate group density (from CO₂ TPD) are given in Table 2. Pd/C E117 and Pd/C Escat exhibited relatively high slurry pH values, indicating the presence of basic surface species. In contrast, Pd/C AA38300 had an acidic slurry pH; the remaining catalysts were neutral (or nearly so). In order to elucidate the pH variation among the catalysts, CO₂ TPD measurements and Na and K analysis by ICP-OES were performed. The CO₂ TPD data are shown in Figure 1(a). The order of CO₂ evolution peak areas was determined as follows: Pd/C E117 ~ Pd/C Escat > Pd/C E101 > Pd/C E199 > Pd/C AA38300 > E117 support. This order is consistent with the slurry pH values shown in Table 2. The amount of CO₂ evolved is related to the amount of carbonate, bicarbonate and carboxylate species on the support surface. The increase in slurry pH observed post-TPD suggests the removal of surface carboxylic acid groups (-COOH) from the AC surface and the decomposition of bicarbonate and carbonate salts on the catalyst surface. Interestingly, high pH catalysts contained large amounts of Na and K and produced CO₂ upon heating in He. This result suggested that accumulating alkali carbonate/bicarbonate salts (Na₂CO₃, K₂CO₃ or NaHCO₃, KHCO₃), which are basic in solution, lead to the pH difference in catalysts. Pd/C E117 and Pd/Calgon had large concentrations of Na and K.
A comparison of H$_2$ TPD peaks for each catalyst is shown in Figure 1 (b). The E117 support material did not exhibit H$_2$ evolution during TPD. All catalysts had small H$_2$ desorption peaks at lower temperatures (<100 °C) associated with Pd and large H$_2$ desorption peaks at higher temperatures (350 °C) associated with hydrogen spillover onto the AC support [19]. Comparing supported Pd on AC and E117 support material, only when Pd particles are present is hydrogen spillover observed. The AC support did not adsorb H$_2$ during reduction. It can be hypothesized that the microporous carbon support “pumps” hydrogen out of the β-hydride phase on Pd particles, and “H leaking” is the first step of the spillover mechanism [20].

High-temperature TPD was performed on the Pd/C E117 catalyst and support, and the results are shown in Figure 2. We infer that the CO$_2$ peak at 270 °C is from the decomposition of bicarbonate species (e.g., NaHCO$_3$ and KHCO$_3$). NaHCO$_3$ can be completely decomposed to Na$_2$CO$_3$, H$_2$O and CO$_2$ at 270 °C (Y. Otsubo, K. Yamaguchi, J. Chem. Soc. Japan, 82, 557-560 (1961)). The catalyst evolved no CO$_2$ beyond 500 °C, which suggested that for this analysis the previous CO$_2$ TPD comparison experiment to 500 °C was sufficient. In contrast, commercial E117 support and Pd/C E117 had great variation of the CO$_2$ evolution peak, which suggested that during the synthesis procedure modifications were made to the carbon support. Pd/C E117 also had one CO$_2$ peak correspond to the decomposition of bicarbonate salt. Catalysts having gone through a reduction and TPD experiment had a higher pH than their unused counterparts, which may have been because the pH of Na$_2$CO$_3$ in solution is greater than the pH of NaHCO$_3$ in solution. After increasing temperature to 800°C, the CO evolution from the catalysts was still incomplete, as evidenced by the asymmetric shape of CO peak.
3.1.2 SA deoxygenation under He

SA deoxygenation at 300 °C for 4 h under He was studied using the various 5 wt. % Pd/C catalyst to elucidate how Pd dispersion, catalyst pH, and H₂ spillover affect performance. The rates of CO₂, CO and H₂ production for semi-batch SA deoxygenation over 5 wt. % commercial Pd catalysts E117, Escat, E101, E199, and AA38300 are plotted in Figure 3. The selectivity to n-C₁₇, CO + CO₂ yield, and CO₂ selectivity are given in Table 3. The reaction went to completion quickly (30 min) over Pd/C E117, with 100% n-C₁₇ yield and 99% CO₂ selectivity. Previous work by Immer et al. showed that E117 is capable of 270 turnovers under He before deactivating (Jeremy prelim 37). Pd/C Escat performed similarly to Pd/C E117: ~83% conversion with high selectivity to n-C₁₇. The eggshell Pd/C (E101 and E199) catalysts behaved similarly to each other: ~43-50% conversion with 95% n-C₁₇ selectivity. E101 was slightly more selective to the decarboxylation pathway with 64.7% CO₂ selectivity, compared with 53.5% for E199. AA38300 reached a higher conversion (~65%) than E101 and E199 with lower CO₂ selectivity. As shown in Figure 3a and table 3, E117 had the highest initial decarboxylation rate at 1.09 mmol/g/h, followed by Escat catalysts with 0.28 mmol/g/h. The initial decarboxylation rate over E101, E199, AA 38300 is very similar (~0.15 mmol/g/h). After 1 h at reaction conditions, only E117 reached full conversion, as its decarboxylation and decarbonylation rates had dropped to zero. Other Pd/AC catalysts showed deactivation of the decarboxylation pathway, but exhibited steady decarbonylation activity, which lead to lower CO₂ selectivity. In Figure 3c it can be seen that E117 initially generated more H₂ than the other Pd/C catalysts. This H₂ may be related to the high decarboxylation activity observed over E117.
Since excess H₂ is evolved during SA deoxygenation under H₂, an additional SA decarboxylation pathway under He resulting in CO₂, H₂ and heptadecenes is proposed

\[ \text{C}_{17}\text{H}_{35}\text{COOH} \rightarrow \text{C}_{17}\text{H}_{34} + \text{CO}_2 + \text{H}_2 \]  

(3)

This stoichiometry can also be derived by adding water-gas-shift (WGS) reaction:

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO} \]  

(4)

to decarbonylation pathway (Eq.2).

Rapid catalyst deactivation was inferred to take place during the first hour of the reaction, particularly for catalytic decarboxylation sites. For Pd on activated carbon, the order of CO₂ selectivity was consistent with the pH of the catalysts: more basic catalysts tended to have higher CO₂ selectivities. As stated previously, accumulation of alkali carbonate/bicarbonate salts on surface was inferred to be responsible for the pH variation; thus, alkali carbonate/bicarbonate salts may have affected the FA deoxygenation pathway. The desired reaction pathway could be obtained via modification of the catalyst with alkali salts.

3.1.3 SA deoxygenation under 5% H₂

Catalyst performance data for semi-batch SA deoxygenation at 300 °C for 4 h under 5% H₂ are summarized in Table 4. The rates of CO₂ and CO production and H₂ consumption for semi-batch SA deoxygenation over various 5 wt. % Pd/C catalysts under 5% H₂ are plotted in Figure 4. Under 5% H₂, E101, E199, and AA 38300 performed more similarly to E117 than under He. E117 was still more active (highest initial and maximum decarboxylation rate with completion about 0.5 h earlier than other Pd/AC catalysts) and more selective to decarboxylation. As shown in Figure 4b and table 4, E117 had the highest initial
The decarboxylation rate to be 1.12 mmol/g/h, which was slightly faster than under He. Escat followed with a decarboxylation rate of 0.59 mmol/g/h. The initial decarboxylation rate over E101, E199, and AA 38300 was very similar, with values from 0.17 to 0.2 mmol/min. Analogous to SA deoxygenation under He, more H\(_2\) was generated initially from E117 than any other Pd/C sample; AA38300 had the most decarboxylation activity. The measured H\(_2\) consumption rate and decarboxylation activity are plotted in Figure 4b. The Pd/C catalysts had CO\(_2\) selectivities of 90-95% and corresponding low values of H\(_2\) consumption. As shown in Figure 4, all Pd/C catalysts initially evolved H\(_2\) coincident with the initial decarboxylation activity. The H\(_2\) consumption peak mirrored the CO production peak. The maximum H\(_2\) consumption rate occurred at the end of each reaction due to the uptake of H\(_2\) upon cooling of the reactor. It was inferred that the consumption of H\(_2\) was related to decarbonylation activity for heptadecene hydrogenation. SA deoxygenation over Pd/C E117 started with H\(_2\) evolution coinciding with the high initial decarboxylation activity. Subsequent H\(_2\) consumption occurred on the trailing edge of the CO\(_2\) peak. E101, E199, and AA 38300 displayed similar decarboxylation activities; however, Pd/C AA38300 exhibited higher decarbonylation activity.

3.2. Lab-Prepared Catalysts

3.2.1 Catalyst Characterization

Based on the above results for commercial 5 wt.% Pd/C catalysts, we proposed that high CO\(_2\) selectivity in SA deoxygenation is related to the slurry pH of catalyst (which is directly related to the quantity of CO\(_2\) desorbed during TPD and the alkali metal content of the catalyst). To test this hypothesis, 2 wt.% and 5 wt. % Pd/C catalysts were prepared using a commercial AC with a high alkali metal content (Calgon, Table 2). In addition, 2 wt.% and 5 wt.% Pd/C
catalysts were synthesized using a high-purity non-porous carbon black (CB) to test the role of support textural properties on deoxygenation performance. The BET surface areas of the Calgon AC and Pd/CB are 1050 and 88 m$^2$/g, respectively. Pd/CB has negligible micropore volume consistent with its specific surface area (Table 1). The total pore volume of Pd/Calgon was less than the other catalysts; therefore, Pd/Calgon has the highest percentage of micropores. The BET surface area and micropore volume of the 5 wt.% Pd/Calgon catalyst are significantly less than those of the Calgon AC, indicating loss of micropores. Although the 5 wt. % Pd/Calgon and Pd/CB were prepared by using same method and Pd precursor, Pd/Calgon has a higher dispersion than Pd/CB. This is likely due to the lower surface area of the CB support. The Pd/Calgon catalysts have a strongly basic slurry pH; whereas, that of Pd/CB is slightly acidic (Table 2).

The CO$_2$ and H$_2$ TPD data for the Pd/Calgon and Pd/CB catalysts are shown in Figure 5. Both Calgon support and Pd/CB did not exhibit H$_2$ evolution peaks during TPD. According to the previous discussion about spill over H$_2$, the absence of TPD peaks for Pd/CB is due to its low surface area and lack of micropores. Thus, the spillover phenomena here essentially involves the Pd metal and a microporous AC support as a receptor. H$_2$ peaks for Pd/Calgon are similar to Pd/C E117. As demonstrated in Fig 5b, 5 wt.% Pd/Calgon has the largest CO$_2$ peak area which is related to its pH and alkali metal content. Pd/CB does not exhibit a significant CO$_2$ peak consistent with the high purity and low surface area of the CB support. The high-temperature TPD data for the 5% Pd/Calgon catalyst and support are shown in Figure 6. There were two CO$_2$ evolution peaks at 270 °C and 650 °C for the Calgon AC support. The large peak at 270°C is likely due to decomposition of bicarbonate species. The CO$_2$ peak at 650°C
might arise from $K_2CO_3$ decomposition. $K_2CO_3$ has a lower decomposition temperature than $Na_2CO_3$, making it more likely that this is the species decomposing at 650°C. Interestingly, the reduced 5 wt.% Pd/Calgon catalyst only exhibits one CO$_2$ peak at 480°C. Low-temperature CO desorption features are observed for the reduced Pd/Calgon catalyst that are not observed for the Calgon support material (Figure 6b).

3.2.2 SA deoxygenation under He

The rates of CO$_2$, CO and H$_2$ production for semi-batch SA deoxygenation using lab-prepared 2 wt.% and 5 wt. % Pd/Calgon and Pd/CB at 300 °C for 4 h under He are plotted in Figure 7. The $n$-heptadecane yield, CO + CO$_2$ yield, CO$_2$ selectivity, initial decarboxylation rate and turnover frequency (TOF) are given in Table 3. In the presence of He, the 5% Pd/Calgon initial rate of decarboxylation is 0.5 mmol/g/min, just less slightly lower than E117 and faster than other commercial samples (Table 3). 5 wt. % Pd/Calgon performed similarly to Pd/C E117 and outperformed any other commercial samples: with 91% $n$-C$_{17}$ yield and 95.7% CO$_2$ selectivity. Due to lower Pd loading, 2 wt. % Pd/Calgon exhibited lower yield and CO$_2$ selectivity, longer completion time and only half initial decarboxylation rate to 5 wt. % Pd/Calgon, but both Pd/Calgon catalysts had CO$_2$ selectivities >90%. Moreover, the Pd/Calgon catalyst also reached full conversion like E117, as its decarboxylation and decarbonylation rates had dropped to zero about same time. In contrast, other Pd/AC catalysts that showed deactivation on decarboxylation but steady decarbonylation activity up to 4 h leading to lower overall CO$_2$ selectivity. Significantly, high H$_2$ production is observed during reaction, we infer that this is due to the high water gas shift activity observed over Pd/Calgon catalysts.
Compared with the Pd/Calgon catalysts, 5% and 2% Pd/CB have both low yields and CO$_2$ selectivity for SA deoxygenation under He (Table 3). There is only 8.4% yield of $n$-C$_{17}$ and near zero initial decarboxylation rate over 5% Pd/CB. According to previous H$_2$ TPD data, we inferred lack of H$_2$ spillover on Pd/CB might be the reason for its inactivity for SA deoxygenation under He. Maier, et al. observed that H$_2$ is essential in the vapor-phase deoxygenation of octanoic acid over Pd/SiO$_2$. This observation led Maier et al. to speculate that "the active catalytic site may not be Pd itself but rather a Pd/H complex"[17]. It was suggested by Immer et al. that catalyst activity in previous liquid-phase SA deoxygenation might be due to hydrogen spillover. The observation of “over Pd/C the selectivity to heptadecenes during reaction is much higher than after the reaction is over.”[14,15] also evidenced the spillover H$_2$ effect. After the spilled over hydrogen was exhausted, the catalyst activity dropped rapidly. Even under such low conversion, Pd/CB still has larger CO peak than Pd/Calgon suggested Pd/CB deoxygenated SA exclusively via the decarbonylation pathway.

3.2.3 SA deoxygenation under 5% H$_2$

Lab-prepared 2% and 5% Pd/Calgon and Pd/CB catalysts performance data at 300 °C for 4 h under 5% H$_2$ are summarized in Table 4. The rates of CO$_2$, CO and H$_2$ production for semi-batch SA deoxygenation are plotted in Figure 8. 5% Pd/Calgon behaved very differently under 5% H$_2$ than under He. The initial decarboxylation rate was 0.07 mmol/g/h under 5% H$_2$, as opposed to 0.5 mmol/g/h under He. Besides, 5% Pd/Calgon exhibited low initial decarbonylation rates, as well as an increased reaction time required for completion, but still selective to decarboxylation pathway with 87% CO$_2$ selectivity. Interestingly, CO evolved over both 2% and 5% Pd/Calgon before CO$_2$, which suggested that the water-gas shift (WGS)
reaction (Equation 4) occurred during the SA deoxygenation reaction. This WGS activity might have been related to the high Na/K concentration on the Calgon carbon support. By reducing Pd loading from 5% to 2%, the initial rate of 2% Pd/Calgon is about half of 5% sample but with similar TOF. The n-heptadecane yield over 2% Pd/Calgon has dropped to 88% compare with 97% over 5% Pd/Calgon and CO₂ selectivity is only 66%. 2% Pd/Calgon also exhibited low initial decarboxylation and decarbonylation rates, and reaction completion time extended to 4 h. The inhibition of decarboxylation pathway over 2% Pd/Calgon under 5% H₂ can be explained by two reason: first, though H₂ may be needed to enhance yields, excess H₂ has been shown to inhibit the decarboxylation pathway [14]. Thus, 2% Pd/CB has richer H/Pd than 5% Pd/Calgon under 5% H₂, and this excess H₂ per Pd site inhibited decarboxylation pathway. Second, similarly to H₂ effect, high initial SA concentration also had inhibition on decarboxylation pathway [13] and 2% Pd/CB has more than twice as much SA/Pd than 5% Pd/Calgon under equivalent reaction condition.

Under 5% H₂, Pd/CB exhibited 70% SA conversion instead of 8% under He, consistent with the hypothesis that H₂ is essential for SA deoxygenation. Low CO₂ selectivity for both 5% and 2% Pd/CB indicates that Pd/CB deoxygenated SA exclusively via the decarbonylation pathway. Compare with Pd/Calgon, Pd/CB had the highest maximum decarbonylation rate, longer reaction completion time and greater H₂ consumption per mole of SA converted, which was consistent with decarbonylation followed by heptadecene hydrogenation. The TOF of 2% and 5% Pd/CB decarbonylation activity was calculated to be 107 and 150 (10³/s) respectively, which is about the same.
4. Conclusion

Under He, Pd/AC catalyst activity to SA decarboxylation was a result of spillover H\textsubscript{2} generated by \textit{in situ} reduction. The combination of Pd and a microporous support is important to spillover mechanism. Only the Pd/AC catalysts demonstrated spillover H\textsubscript{2}. The activated carbon support and Pd/CB (nonporous support) didn’t have any H\textsubscript{2} evolution peak. Pd/CB was inactive for SA decarboxylation, showing almost exclusively decarbonylation activity. For Pd/AC, catalytic deoxygenation of SA occurred primarily via decarboxylation, yielding \textit{n}-C\textsubscript{17} and heptadecenes. H\textsubscript{2} was evolved concomitant with CO\textsubscript{2} and CO during the reaction. The initial H\textsubscript{2} evolution peak coincided with the high initial decarboxylation activity, which might be related to the water-gas shift (WGS) reaction. The basic catalysts Pd/C E117 and Pd/Calgon with high Na/K concentrations showed the highest decarboxylation activity among the Pd/AC catalysts. Alkali salts were assumed to be carbonate of bicarbonate salts. Under 5% H\textsubscript{2}, Pd/AC and Pd/CB both had high SA conversion, but Pd/CB was selective to decarbonylation, which was attributed to the nonporous support. Pd/Calgon had low initial and maximum decarboxylation rate and a longer completion time for the reaction. Due to CO generation prior to CO\textsubscript{2} over Pd/Calgon, WGS activity was assumed to exist.
References


4. A.J. Cavallo, Predicting the peak in world oil production, Natural Resources Research vol. 11, No. 3 (2002), 187-195


20. C. I. Contescu, and V. V. Bhat; *American Chemistry Society: Division of Fuel Chemistry*. 2009, 54(1), 382
### Table 1: Catalyst characterization results.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pd Dispersion&lt;sup&gt;a&lt;/sup&gt; (%)</th>
<th>H/Pd TPHD (mol/mol)</th>
<th>Micropore Volume (cm&lt;sup&gt;3&lt;/sup&gt;/g)</th>
<th>Total pore Volume (cm&lt;sup&gt;3&lt;/sup&gt;/g)</th>
<th>BET surface area (m&lt;sup&gt;2&lt;/sup&gt;/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% Pd/C E117</td>
<td>14.7</td>
<td>0.53</td>
<td>0.21</td>
<td>0.62</td>
<td>855</td>
</tr>
<tr>
<td>5% Pd/C Escat</td>
<td>15.5</td>
<td>0.48</td>
<td>0.21</td>
<td>0.63</td>
<td>825</td>
</tr>
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<td>5% Pd/C E101</td>
<td>28.8</td>
<td>0.38</td>
<td>0.20</td>
<td>0.74</td>
<td>854</td>
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<tr>
<td>5% Pd/C E199</td>
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<td>0.24</td>
<td>0.21</td>
<td>0.77</td>
<td>799</td>
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<tr>
<td>5% Pd/C AA38300</td>
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<td>0.25</td>
<td>0.17</td>
<td>0.68</td>
<td>810</td>
</tr>
<tr>
<td>5% Pd/C Calgon*</td>
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<td>0.23</td>
<td>0.38</td>
<td>736</td>
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<td>2% Pd/C Calgon*</td>
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<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5% Pd/CB*</td>
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<td>0.0061</td>
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<tr>
<td>2% Pd/CB*</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>E117 support</td>
<td>-</td>
<td>-</td>
<td>0.23</td>
<td>0.72</td>
<td>871</td>
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<tr>
<td>Calgon support</td>
<td>-</td>
<td>-</td>
<td>0.40</td>
<td>0.49</td>
<td>1050</td>
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<sup>a</sup>CO chemisorption assuming a 1:1.5 CO:Pd surface atom stoichiometry

<sup>*</sup>Lab prepared catalysts, Pd(NO<sub>3</sub>)<sub>2</sub> precursor
Table 2. Catalyst characterization results (continued).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>pH</th>
<th>CO₂ TPD (mmol/g)</th>
<th>pH Post TPD</th>
<th>Conc. of Na -mg/kg-</th>
<th>Conc. of K -mg/kg-</th>
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</thead>
<tbody>
<tr>
<td>5% Pd/C E117</td>
<td>9.3</td>
<td>0.092</td>
<td>11.4</td>
<td>8739</td>
<td>30.2</td>
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<tr>
<td>5% Pd/C Escat</td>
<td>8.1</td>
<td>0.105</td>
<td>10.5</td>
<td>854</td>
<td>12.1</td>
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<td>5% Pd/C E101</td>
<td>7.5</td>
<td>0.063</td>
<td>9.2</td>
<td>723</td>
<td>ND</td>
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<tr>
<td>5% Pd/C E199</td>
<td>7.1</td>
<td>0.052</td>
<td>8.9</td>
<td>557</td>
<td>ND</td>
</tr>
<tr>
<td>5% Pd/C AA38300</td>
<td>5.3</td>
<td>0.064</td>
<td>7.1</td>
<td>81.5</td>
<td>ND</td>
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<tr>
<td>5% Pd/C Calgon*</td>
<td>10.5</td>
<td>0.135</td>
<td>10.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2% Pd/Calgon*</td>
<td>10.1</td>
<td>0.095</td>
<td>10.6</td>
<td>-</td>
<td>-</td>
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<tr>
<td>5% Pd/CB*</td>
<td>6.3</td>
<td>0.003</td>
<td>7.0</td>
<td>-</td>
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<tr>
<td>2% Pd/CB*</td>
<td>6.5</td>
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<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>E117 support</td>
<td>7.1</td>
<td>0.03</td>
<td>7.5</td>
<td>95</td>
<td>164</td>
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<td>Calgon support</td>
<td>11.0</td>
<td>0.04</td>
<td>-</td>
<td>2134</td>
<td>9871</td>
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*Lab prepared catalysts, Pd(NO₃)₂ precursor
Table 3. SA deoxygenation over Pd/C catalysts at 300°C and 15 atm under He.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Initial Decarboxylation Rate (mmol/g/h)</th>
<th>TOF (10^3/s)</th>
<th>n-C&lt;sub&gt;17&lt;/sub&gt; Yield (%)</th>
<th>n-C&lt;sub&gt;17&lt;/sub&gt; Selectivity (%)</th>
<th>CO + CO&lt;sub&gt;2&lt;/sub&gt; Yield (%)</th>
<th>CO&lt;sub&gt;2&lt;/sub&gt; Selectivity (%)</th>
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</thead>
<tbody>
<tr>
<td>5% Pd/C E117</td>
<td>1.09</td>
<td>264</td>
<td>100</td>
<td>97.7</td>
<td>99.5</td>
<td>98.9</td>
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<tr>
<td>5% Pd/C Escat</td>
<td>0.28</td>
<td>65.1</td>
<td>83.7</td>
<td>98.3</td>
<td>76.8</td>
<td>89.8</td>
</tr>
<tr>
<td>5% Pd/C E101</td>
<td>0.14</td>
<td>76.3</td>
<td>44.3</td>
<td>93.6</td>
<td>49.8</td>
<td>64.7</td>
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<tr>
<td>5% Pd/C E199</td>
<td>0.16</td>
<td>16.6</td>
<td>42.9</td>
<td>95.8</td>
<td>47.7</td>
<td>53.5</td>
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<tr>
<td>5% Pd/C AA38300</td>
<td>0.11</td>
<td>10.9</td>
<td>64.8</td>
<td>94.4</td>
<td>60.3</td>
<td>38.4</td>
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<tr>
<td>5% Pd/C Calgon*</td>
<td>0.49</td>
<td>70.6</td>
<td>91.3</td>
<td>98.5</td>
<td>83.8</td>
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<td>2% Pd/C Calgon*</td>
<td>0.19</td>
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<td>89.8</td>
<td>99.3</td>
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<tr>
<td>5% Pd/CB*</td>
<td>0.001</td>
<td>0.06</td>
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<td>98</td>
<td>15.6</td>
<td>0.5</td>
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<tr>
<td>2% Pd/CB*</td>
<td>-</td>
<td>-</td>
<td>14.2</td>
<td>88.6</td>
<td>15.0</td>
<td>17.4</td>
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</table>

*Lab prepared catalysts, Pd(NO<sub>3</sub>)<sub>2</sub> precursor
Table 4. SA deoxygenation over Pd/C catalysts at 300°C and 15 atm under 5% H₂.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Initial Decarboxylation Rate (mmol/g/min)</th>
<th>TOF (10³/s)</th>
<th>n-C₁₇ Yield (%)</th>
<th>CO + CO₂ Yield (%)</th>
<th>CO₂ Selectivity (%)</th>
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<tbody>
<tr>
<td>5% Pd/C E117</td>
<td>1.12</td>
<td>271</td>
<td>100</td>
<td>96</td>
<td>95.2</td>
</tr>
<tr>
<td>5% Pd/C Escat</td>
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<td>98.2</td>
<td>87.6</td>
<td>97.3</td>
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<tr>
<td>5% Pd/C E101</td>
<td>0.61</td>
<td>76.3</td>
<td>105</td>
<td>100.1</td>
<td>93.5</td>
</tr>
<tr>
<td>5% Pd/C E199</td>
<td>0.79</td>
<td>78.8</td>
<td>102.9</td>
<td>99.2</td>
<td>93.6</td>
</tr>
<tr>
<td>5% Pd/C AA38300</td>
<td>0.70</td>
<td>65.7</td>
<td>110.6</td>
<td>101.1</td>
<td>90.8</td>
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<tr>
<td>5% Pd/C Calgon*</td>
<td>0.07</td>
<td>10.1</td>
<td>97.7</td>
<td>88.4</td>
<td>87.9</td>
</tr>
<tr>
<td>2% Pd/C Calgon*</td>
<td>0.02</td>
<td>7.3</td>
<td>88.2</td>
<td>75</td>
<td>66.5</td>
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<tr>
<td>5% Pd/CB*</td>
<td>0.01</td>
<td>1.7</td>
<td>71.3</td>
<td>77</td>
<td>6.7</td>
</tr>
<tr>
<td>2% Pd/CB*</td>
<td>-</td>
<td>-</td>
<td>72</td>
<td>80.6</td>
<td>7.0</td>
</tr>
</tbody>
</table>

*Lab prepared catalysts, Pd(NO₃)₂ precursor
Figure 1. TPD (4°C/min, He) comparison of commercial catalysts and E117 support: (a) H₂ and (b) CO₂.
Figure 2. TPD (10°C/min, He) comparison of Pd/C (E117) and E117 support: (a) CO$_2$ and (b) CO.
Figure 3. On-line QMS results for SA deoxygenation over commercial Pd/C catalysts at 300°C and 15 atm under He: (a) CO₂, (b) CO, and (c) H₂.
(a)
Figure 4. On-line QMS results for SA deoxygenation over commercial Pd/C catalysts at 300 °C and 15 atm under 5% H\textsubscript{2}: (a) CO\textsubscript{2}, (b) CO and H\textsubscript{2}
(a)
(b)
Figure 5: TPD (TPD (4°C/min, He) comparison of Pd/Calgon catalysts and Calgon carbon support: (a) H₂ and (b) CO₂.
Figure 6: TPD (10°C/min, He) comparison of Pd/Calgon catalysts and Calgon carbon support: (a) CO$_2$ and (b) CO.
Figure 7. On-line QMS results for SA deoxygenation over Lab-prepared catalysts at 300°C and 15 atm under 5% H₂: (a) CO₂, (b) CO, and (c) H₂
mmol/min CO₂

Batch Time (h)

(a)
(c)

- 5% Pd/CB
- 2% Pd/CB
- 5% Pd/Calgon
- 2% Pd/Calgon
Figure 8. On-line QMS results for SA deoxygenation over Lab-prepared catalysts at 300°C and 15 atm under 5% H₂: (a) CO₂, (b) CO, and H₂
Summary and Outlook

Keyi Sun
Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695-7905, USA
Summary

Catalytic deoxygenation of fatty acids (FAs) to hydrocarbons allows the conversion of lipid biomass to "drop-in" replacements for petroleum-derived transportation fuels. In this dissertation, FA deoxygenation reactions were investigated in both the vapor and liquid phases using supported Pd catalysts. Steady-state catalytic deoxygenation of octanoic acid (OA) was investigated at 260ºC and 1 atm using a fixed bed micro-reactor with on-line gas chromatography. Semi-batch deoxygenation of stearic acid (SA) in dodecane at 300ºC and 15 atm was investigated using a stirred autoclave reactor with on-line quadrupole mass spectrometry (QMS). The catalysts were characterized by transmission electron microscopy (TEM), CO chemisorption, temperature-programmed desorption (TPD), temperature-programmed hydride decomposition (TPHD), and diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS). Herein, improved catalysts and optimized reaction conditions are identified that advance the commercial potential of this technology and begin to elucidate the underlying reaction mechanism(s). These fundamental studies are crucial to the eventual commercialization of this biofuel technology.

Key characteristics of the supported Pd catalyst are summarized below:

1. Pd particle size

Pd particle size effects were investigated using Pd/SiO₂ catalysts prepared by two different methods: incipient wetness (IW) and ion exchange (IE). The 1.78 wt.% Pd/SiO₂ (IW) catalyst contained 7.5-nm Pd nanoparticles with predominantly <100> facets, as evidenced by high-angle annular dark-field scanning TEM and DRIFTS of adsorbed CO (νCO = 1990 cm⁻¹). The 0.6 wt.% Pd/SiO₂ (IE) catalyst contained 1.5-nm Pd clusters that exhibited strong linear and...
bridging $v_{\text{CO}}$ bands ($v_{\text{CO}} = 2100$ and $1930$ cm$^{-1}$, respectively). When these catalysts were employed for OA deoxygenation under 10% H$_2$ at 260ºC and 1 atm, the Pd/SiO$_2$ (IE) catalyst deactivated rapidly and irreversibly due to self-poisoning by CO and strongly adsorbed OA. In contrast, the Pd/SiO$_2$ (IW) catalyst deactivated less rapidly and could be regenerated by simply heating in H$_2$ to remove OA residues.

2. Alloying with Au

Bimetallic catalysts have attracted great attention because of their enhanced performance, as compared with their monometallic counterparts. Among the various bimetallic catalysts, Pd-Au has been intensively investigated and employed as catalyst in many important applications [1]. In our research, addition of Au to Pd/SiO$_2$ was found to improve catalyst stability without significantly reducing catalytic activity. The geometric and electronic effects of alloying Pd with Au produced weaker interactions between CO and Pd surface sites (including isolated atoms and multi-atom ensembles) and mitigated catalyst deactivation by self-poisoning. For Pd-Au alloys, there is a geometric effect: Active Pd ensembles are diluted by inactive Au, and eventually all Pd atoms are isolated by Au. An electronic effect, charge transfer between Pd and Au, helps to explain why Au is able to isolate Pd. Au accepts $s$ and $p$ electrons from Pd and donates $d$ electrons to Pd, and this results in a more atom-like electron configuration for Pd atoms on PdAu alloy surfaces.

3. Support effects

FA deoxygenation can be achieved by decarboxylation or decarbonylation. FA decarboxylation is preferred since, in principle, this reaction pathway does not require an external source of H$_2$ to produce the desired alkane product. Semi-batch deoxygenation of SA
in dodecane at 300ºC and 15 atm was employed to screen supported Pd catalysts for decarboxylation selectivity and activity. Three (3) types of supported Pd catalysts were investigated: Pd on silica (Pd/SiO$_2$), Pd on activated carbon (Pd/AC), and Pd on carbon black (Pd/CB). The AC supports have very high surface areas (800-1000 m$^2$/g) and are microporous. The SiO$_2$ support (~300 m$^2$/g) has a high mesopore volume, and the CB support (88 m$^2$/g) is essentially non-porous. Pd/AC catalysts exhibit significant FA decarboxylation activity. In contrast, Pd/SiO$_2$ and Pd/CB catalysts show only decarbonylation activity. Moreover, microporous carbon supports were shown to promote H spillover from Pd nanoparticles during in situ catalyst reduction, and adsorbed H is essential to the FA deoxygenation reaction (vide infra).

4. Alkali promoters

Decarboxylation activity was found to be related to the pH of the Pd/AC catalysts. More basic catalysts showed the highest decarboxylation activity among the commercial Pd/AC catalysts evaluated in this study. Interestingly, high pH catalysts contained large amounts of Na and K and produced CO$_2$ upon heating in He (TPD). This result suggested that the presence of alkali carbonate/bicarbonate salts (Na$_2$CO$_3$, K$_2$CO$_3$ or NaHCO$_3$, KHCO$_3$), which are basic in solution, led to higher pH of these catalysts, and these alkali metals may act as catalyst promoters, influencing the FA deoxygenation pathway.

In addition to the catalyst design, optimum reaction conditions were identified.

5. H$_2$ partial pressure

Although H$_2$ is not required by the reaction stoichiometry for FA decarboxylation, it was proven to be essential for OA deoxygenation under steady-state conditions. The presence of
adsorbed hydrogen favors hydrogenation of surface alkenyl groups and prevents rapid and irreversible catalyst deactivation; however, under high H$_2$ partial pressures, the decarboxylation pathway is inhibited, and only decarbonylation is observed. Work of Lamb and Whitten on the mechanism of butanoic acid decarboxylation on Pd(111) indicated that adsorbed H influences reaction barriers and reference energies by competing with O for Pd electrons [2]. Higher H$_2$ partial pressures promote the decarbonylation pathway by favoring OA hydrogenation to octanal; however, the increased decarbonylation activity cannot compensate the lost decarboxylation activity, and OA conversion declines as H$_2$ partial pressure increases.

In the liquid phase, transient catalytic activity for SA deoxygenation under He was shown to be related to hydrogen spillover from Pd to the AC support during in situ catalyst reduction. Pd/CB was inactive for SA decarboxylation under He, showing almost exclusively decarbonylation activity. The combination of Pd and a microporous support are important to the spillover mechanism. It has been hypothesized that the microporous carbon support “pumps” hydrogen out of the Pd β-hydride phase, and “H leaking” is the first step of the spillover mechanism [3]. Only Pd/AC catalysts evidenced hydrogen spillover in TPD. The AC support (without Pd) and Pd/CB (non-porous support) do not exhibit a high-temperature H$_2$ evolution peak due to recombination of spilled over H atoms. High H$_2$ partial pressures during SA deoxygenation inhibited the decarboxylation pathway, as was observed for OA deoxygenation in the vapor phase. A relatively low H$_2$ partial pressure (5%-10% at 15 atm) favors the decarboxylation pathway and gives high FA deoxygenation activity.
6. Reaction Kinetics

In the vapor-phase, OA deoxygenation kinetics data were obtained at steady-state by varying the weight hourly space velocity (WHSV) (while holding the OA mole fraction constant) and measuring the resultant OA conversion (X). Plotting \( \ln(1-X) \) versus \( 1/\text{WHSV} \) gives a highly correlated linear fit indicating that the reaction is first order in OA concentration under these conditions. Using the OA concentration in the feed to determine the zero-conversion rate, the turnover frequency (TOF) of 5 wt. % Pd/C (E117) for OA deoxygenation is 0.026 s\(^{-1}\) at 260°C and 1 atm.

In the liquid phase, in order to derive reaction kinetics from the on-line QMS data, it was necessary to relate the measured product partial pressure in the reactor effluent to the reaction rate. The initial decarboxylation rate was calculated from the initial slope of a \( P_{\text{CO}_2} \) vs. \( t \) plot (obtained using linear regression). The TOFs of commercial 5 wt.% Pd/AC catalysts for SA deoxygenation under 5% H\(_2\) ranged from 0.07-0.26 s\(^{-1}\) at 300°C and 15 atm.

Outlook

To summarize, in order to get optimal results for FA deoxygenation, catalysts should be designed using Pd or Pd alloys with a less active metal (Au, Cu) in the form of relatively large nanoparticles (5-7 nm) on a basic AC support. The desired decarboxylation reaction pathway may be promoted via modification of a neutral Pd/AC catalyst with alkali metal salts. To test this hypothesis, a lab-prepared 5 wt.% Pd/AC catalyst was obtained by incipient wetness impregnation of a neutral AC support (with low alkali metal content) using an aqueous solution of Pd(NO\(_3\))\(_2\). The resultant material was dried in air at 80°C overnight and then reduced \textit{ex situ} at 300 °C in flowing H\(_2\) for 1 h. Subsequently, one-half of the Pd/AC catalyst was treated with
1 wt.% NaHCO₃ to produce a Na-promoted Pd/AC catalyst. The Na and K concentrations in the lab-prepared catalysts are given in Table 1. As shown in Fig. 1, under both He and 5% H₂, the Na-promoted Pd/AC catalyst has much higher decarboxylation activity than the neutral Pd/AC catalyst. It is concluded that by adding alkali promoters, activity and reaction selectivity to decarboxylation are increased. Since the silica-supported bimetallic PdAu alloy improves catalyst stability by mitigating self-poisoning, other (less expensive) bimetallic catalysts could be prepared in the future. For example, supported PdCu catalysts are a recommended topic for future research.
References

4. C. I. Contescu, and V. V. Bhat; American Chemistry Society : Division of Fuel Chemistry. 2009, 54(1), 382
Table 1. Lab prepared catalysts Na and K concentration.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Na (mg/kg)</th>
<th>K (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% Pd/C E117*</td>
<td>95</td>
<td>64</td>
</tr>
<tr>
<td>Na-promoted 5% Pd/C E117*</td>
<td>~10000</td>
<td>64</td>
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</tbody>
</table>

*Lab prepared catalysts, Pd(NO$_3$)$_2$ precursor
Figure 1. On-line QMS CO and CO\textsubscript{2} results for SA deoxygenation over Na-promoted and unpromoted Pd/C catalysts at 300\textdegree C and 15 atm under: (a) He (b) 5\% H\textsubscript{2}.