Vapor Phase Deoxygenation of Heptanoic Acid over Silica-Supported Palladium and Palladium-Tin Catalysts

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Abstract

Silica-supported Pd and PdSn catalysts were prepared by ion exchange or incipient wetness impregnation and characterized with H_2 chemisorption, X-ray diffraction, in situ Sn K-edge X-ray absorption near edge structure (XANES), and transmission electron microscopy. The activity of the catalysts was evaluated in the deoxygenation of vapor-phase heptanoic acid at 0.1 MPa and 573 K. A Pd catalyst synthesized via ion exchange formed nanoparticles of 1.1 ± 0.4 nm and was more stable in heptanoic acid conversion compared to a Pd catalyst synthesized via incipient wetness impregnation having nanoparticles of 2.4 ± 0.5 nm. The addition of Sn to a Pd catalyst by either co-impregnation of precursors or physical mixing of supported monometallic catalysts improved the overall catalyst stability. Moreover, Sn addition expanded the reaction network from primarily decarbonylation over Pd to include dehydration and decarboxylative ketonization over PdSn. Electron microscopy confirmed the physical migration of Sn during catalytic reaction. In situ XANES analysis during the deoxygenation of a carboxylic acid suggests that partially reduced SnO_x is the active Sn phase associated with Pd nanoparticles under reaction conditions.

Key words: Pd; Sn; bimetallic heterogeneous catalysts; physical mixture; deoxygenation; carboxylic acids; migration

1. Introduction

Biomass is a promising alternative feedstock to petroleum and other fossil carbon sources that is both renewable and readily available.^{1–3} Biomass-derived molecules often contain a significantly higher oxygen content compared to molecules obtained from fossil resources. Therefore, oxygen must be selectively removed from those biomass-derived compounds to produce chemicals and fuels. This can be accomplished via several classes of chemical reactions including decarbonylation, decarboxylation, decarboxylative ketonization, and dehydration.^{4–7}

Interest in the deoxygenation of biomass-derived organic acids has increased because of a higher demand for biodiesel.⁸ Hydrocarbons can be produced via decarboxylation and decarbonylation of carboxylic acids. Snåre et al. investigated a wide variety of metal catalysts for the transformations, utilizing stearic acid as the model carboxylic acid to produce the diesel-like molecule n-heptadecane at 573 K.⁴ Continuous flow experiments revealed that Pd/C and Pt/C catalysts deactivate rapidly during deoxygenation reactions utilizing lauric acid as the model acid,⁹ depending on the concentration of carboxylic acid in the feed. Faster deactivation occurred when greater concentrations of lauric acid contacted the catalyst. The specific cause of catalyst deactivation, however, is not clear. Mäki-Arvela et al. concluded that coking occurs⁹ while others indicate that the carbonaceous species on the catalyst surface are not associated with traditional coke.^{10,11} Ping et al. reported that the decrease in the rate of decarbonylation of stearic acid over Pd/SiO₂ results from the adsorption of stearic acid on active sites together with adsorption of unsaturated products and CO.¹⁰

Sun et al. recently demonstrated how the stability of Pd catalysts used in deoxygenation reactions in 10% H₂/He at 533 K depends on the Pd particle size and alloying.¹¹ Larger Pd particles were more stable for the deoxygenation of octanoic acid and alloying Pd with Au further improved the stability of the catalyst.

Recent work by Lopez-Ruiz et al. targeted high value alpha olefins formed by the decarbonylation of concentrated heptanoic acid without co-feeding dihydrogen.¹² Alpha olefins are valuable commodity chemicals used in the production of plastics, synthetic lubricants, surfactants, and other materials. Carbon-supported Pt and Pd catalysts were shown to be active for the decarbonylation of heptanoic acid but suffered from rapid deactivation at 573 K and atmospheric pressure.^{12,13} Low selectivity to 1-hexene at high conversions was observed for all tested conditions. Indeed, 20% selectivity to the desired alpha olefin product was only achieved at conversions below 10% under vapor phase conditions. The majority of products consisted of internal hexene isomers formed by the rapid isomerization of 1-hexene.

Previous work has shown that Sn can be a beneficial additive to metal catalysts for a range of chemical reactions.^{14–20} Electronic effects have been observed in metal-Sn alloys resulting in a decreased heat of adsorption for CO.²¹ These reported electronic effects may help decrease the rate of deactivation due to self-poisoning.²² Furthermore, Chiappero et al. have demonstrated that Pt alloyed with Sn can improve the selectivity to alpha olefins formed during the deoxygenation of methyl esters under semi-batch conditions at temperatures ranging from 593 K to 623 K and pressures ranging from 0.2 MPa to 1.14 MPa.²³ Alpha olefin selectivity improved from 6.5% over Pt to 23% over PtSn at 623 K.

In the present study, vapor phase deoxygenation of heptanoic acid was investigated over Pd and PdSn catalysts. In particular, the stability of the catalysts and the selectivity to higher value products without co-fed dihydrogen were explored. Physical mixtures and two stage catalyst beds were also examined to probe the influence of Sn proximity on the reactivity of Pd nanoparticles. Advanced microscopy techniques and X-ray absorption near-edge structure (XANES) spectroscopy were utilized to characterize the catalysts.

2. Experimental Methods

2.1 Catalyst synthesis

Two Pd/SiO₂ catalyst samples of nominally 5 wt% each were prepared by ion exchange (IE) or incipient wetness impregnation (IWI) of the Pd precursor using Davisil 636 silica (Sigma-Aldrich) as a support. A high dispersion Pd/SiO₂ sample, denoted as Pd/SiO₂-H, was synthesized via IE using methods modified from a previously described procedure.²⁴ For example, the PdCl₂ precursor (0.510g, 99%, Sigma-Aldrich) was dissolved in a solution of aqueous ammonia (5.428 cm³ ammonium hydroxide, ACS plus, Fisher Scientific, in 282 cm³ distilled deionized water). The metal solution was added dropwise over 10 min to 5.70 g of acid-washed Davisil 636 silica in 114 cm³ of distilled deionized water at 343 K. The metal salt and silica slurry was stirred for 60 min at 343 K, and then cooled to room temperature. The mixture was washed with water and vacuum dried overnight. After calcination in flowing air (medical grade, GTS-Welco) at 673 K for 2 h, the sample was pre-reduced in flowing H₂ (99.999%, GTS-Welco) at 623 K for 2 h. A low dispersion Pd/SiO₂ sample, denoted as Pd/SiO₂-L, was prepared via incipient wetness impregnation (IWI) with 10 wt% Pd(NO₃)₂•4NH₃ in H₂O (99.99%, Sigma-Aldrich), which was further diluted in water prior to impregnation. The sample was calcined in flowing air (medical grade, GTS-Welco) at 673 K for 2 h, and pre-reduced at 623 K in flowing H₂ (99.999%, GTS-Welco) for 2 h.

A Sn/SiO₂ catalyst sample with nominally 5.6 wt% Sn was also prepared by IWI using SnCl₂ (98%, Sigma Aldrich) dissolved in water, calcined in flowing air (medical grade, GTS-Welco) at 673 K for 2 h and pre-reduced at 623 K in flowing H₂ (99.999%, GTS-Welco) for 2 h.

Two types of PdSn/SiO₂ samples were prepared. First, Sn was chemically added to a Pd/SiO₂-H sample containing nominally 2.5 wt% Pd by the incipient wetness impregnation method using an aqueous solution of SnCl₂. After Sn impregnation, the PdSn sample was calcined and pre-reduced using the same procedure as the Sn/SiO₂ catalyst. This chemically-mixed sample was denoted as PdSn/SiO₂-C. The chemically-mixed Pd-Sn/SiO₂-C sample was prepared with a 1:1 atomic ratio of Pd:Sn having a nominal Pd loading of 2.5 wt% and a nominal Sn loading of 2.8 wt%. To prepare a second Sn and Pd

loaded catalyst, the Sn/SiO₂ sample (5.6 wt% Sn) was mechanically mixed with the Pd/SiO₂-H until a uniform mixture was produced. The physically-mixed bimetallic catalyst, denoted as PdSn/SiO₂-P, was prepared with a 1:1 atomic ratio of Pd:Sn having a nominal Pd loading of 2.5 wt% and a Sn loading of 2.8 wt%. All thermal treatments utilized a temperature ramp rate of 1 K min⁻¹.

2.2 Dihydrogen chemisorption

The number of available metal surface sites was determined using H₂ chemisorption on a Micromeritics ASAP 2020 adsorption system. Each catalyst sample was evacuated for 10 h at 573 K followed by reduction at 623 K in flowing H₂ (99.999%, GTS-Welco) for 1 h. After reduction, the system was evacuated and cooled to 373 K for analysis. The number of available metal sites was determined by extrapolating the high pressure, linear portion of the isotherm to zero pressure. At 373 K, the stoichiometric ratio of H to surface Pd is 1:1.^{13,25}

2.3 X-ray diffraction

Powder X-ray diffraction (XRD) patterns were measured on a PANalytical X'Pert Pro equipped with monochromatic Cu K α -radiation (λ =1.54056 Å) using a step size of 0.0167113°.

2.4 Transmission electron microscopy

The high resolution transmission electron microscopy (HR-TEM) and scanning transmission electron microscopy (STEM) utilized in the line scan analysis and energy dispersive spectroscopy (STEM-EDS) maps were performed on an FEI Titan 80-300 operating at 300 kV that is equipped with a Gatan 794 Multi-scan Camera (EFTEM) and an energy dispersive spectrometer for X-ray elemental analysis. Samples analyzed on the FEI Titan 80-300 were prepared by dispersing catalyst samples in cyclohexane and mounted on holey carbon grids.

Samples for selected area EDS composition analysis were dispersed in ethanol and mounted on holey carbon grids for examination in a JEOL 2010F 200 kV scanning transmission electron microscope equipped with an Oxford Aztec Energy Dispersive System for elemental analysis. Images were recorded in high angle annular dark field (HAADF) mode. Elemental compositions were acquired in selected regions of the sample, as indicated by "boxes" shown in the HAADF-STEM image.

2.5 X-ray absorption near-edge structure

The in situ Sn K-edge X-ray absorption near-edge structure (XANES) analysis during temperature programmed reduction (TPR) in H_2 was conducted at the 8C beamline in the Pohang Light Source (PLS) operating with a 3.0 GeV ring energy and a 300 mA ring current. A Si (1 1 1) double crystal monochromator was employed to vary the X-ray photon energy. The XANES spectra were obtained in the transmission mode using ionization gas chambers to detect the primary (I_o , 100% N_2) and the transmitted (I_t , 70% N_2 , balance Ar) beam intensities. Higher order harmonic contamination was eliminated by detuning the monochromator to reduce the incident X-ray intensity by about 30%. Energy calibration was performed using a standard Sn foil. A self-supported catalyst wafer was loaded into an in situ quartz reactor with a 25.4 mm external diameter. A quartz sample holder with a 15 mm external diameter was positioned in the center of the reactor with a thermocouple port located just about the sample. A mixture of 5% H_2 in He flowed at $100\text{ cm}^3\text{ min}^{-1}$ while the temperature ramped at 5 K min^{-1} from room temperature to 673 K. The catalysts examined by XANES were unreduced samples of Sn/SiO_2 , $PdSn/SiO_2\text{-C}$, and $PdSn/SiO_2\text{-P}$. The relative white line intensity of each Sn sample during H_2 -TPR was calculated on the basis of the normalized edge jump of Sn foil using: $I_r = I(\text{SnOx sample}) / I_o(\text{Sn foil})$.

The in situ Sn K-edge XANES spectra were also collected during butyric acid (99+%, Alfa Aesar) deoxygenation at the same beamline. Butyric acid was chosen as the probe molecule because of its high vapor pressure relative to heptanoic acid. A catalyst sample was pressed into a wafer that was placed

directly in the quartz sample holder described above and reduced in situ in $100\text{ cm}^3\text{ min}^{-1}$ 5% H_2/He during a heating ramp of 10 K min^{-1} to a temperature of 623 K, after which the temperature was constant for 30 min before cooling to the reaction temperature of 573 K. Dinitrogen flowing at $500\text{ cm}^3\text{ min}^{-1}$ was bubbled through liquid butyric acid maintained at room temperature and the mixture was fed to the catalyst held at 573 K for XANES collection. The TPR results were processed using WinXAS 3.1 software and the in situ deoxygenation reaction results were processed using Athena software.

2.6 Catalytic deoxygenation of heptanoic acid

Catalysts were evaluated for activity in the deoxygenation of heptanoic acid in a continuous upward flow reactor as described previously.¹² In summary, the reactor consisted of a 0.64 cm OD x 0.089 cm wall thickness stainless steel tube that is 15 cm in length. A pre-heating section of the same material was 10 cm in length. Glass wool was placed above and below the catalyst to maintain the position of the bed. Aluminum heating jackets surrounded the reactor and pre-heating section to facilitate uniform heat transfer.

A liquid feed consisting of 95 wt% heptanoic acid (>98%, Sigma-Aldrich) and 5 wt% dodecane (>99%, Sigma-Aldrich) was pumped from an ISCO 500D syringe pump into the pre-heating section where the feed was vaporized. Dodecane was included in the feed as an internal standard.

The catalysts were reduced in situ with $150\text{ cm}^3\text{ min}^{-1}$ H_2 (99.999%, GTS-Welco) at 623 K for 2 h after heating with a ramp rate of 1 K min^{-1} . The reactor was then cooled to 573 K and purged with $200\text{ cm}^3\text{ min}^{-1}$ N_2 (99.999%, GTS-Welco) for 1 h.

Liquid-phase products were separated in a condenser positioned above the outlet of the reactor. Initial time on stream was defined as the time which liquid began to enter the condenser. Gaseous products were continuously removed by a $7\text{ cm}^3\text{ min}^{-1}$ purge of N_2 (99.999%, GTS-Welco) through the condenser and fed to an on-line HP 5890 Series II gas chromatograph equipped with a

ShinCarbon 80/100 packed column and a thermal conductivity detector (TCD). Liquid-phase products were analyzed using an Agilent 7890 gas chromatograph equipped with a ZB-FFAP column and a flame ionization detector (FID).

Using the mass transfer criteria on the conversion of heptanoic acid over supported Pt catalysts described in a previously published paper¹², we verified the lack of internal and external mass transfer effects on the measured rates over the supported PdSn/SiO₂ catalysts used in the current work.

2.7 Calculation of rates and selectivity

Conversion was defined as the total rate of formation of the deoxygenation products divided by the molar feed rate of reagent as shown in Eq. 1. In this work, conversion was always less than 20%.

$$\text{Conversion} = \frac{(\text{total molar formation rate of hexane} + 1\text{-hexene} + i\text{-hexene} + \text{heptanal} + \text{hexadiene} + 2 * \text{tridecanone} + \text{unknown})}{(\text{molar rate of heptanoic acid fed})} \quad (1)$$

A blank run with SiO₂ support revealed a background conversion that was below 0.1%, and thus background conversion was neglected in this study. The reaction rate over monometallic Pd catalysts was reported as a turnover frequency (TOF), or reaction rate normalized by the number of available surface sites, to properly account for the difference in Pd particle size between the samples. We assumed that the particle size of the active Pd catalyst was equal to the size measured on fresh catalyst sample. The TOF (s⁻¹) is therefore calculated according to Eq. 2.

$$\text{TOF} = \text{Conversion} * \frac{\text{molar rate of heptanoic acid fed}}{\text{moles of surface metal}} \quad (2)$$

Liquid product selectivities were defined by molar rates of product formation divided by total molar rate of formation of all products as shown in Eq. 3.

$$\text{Selectivity} = \frac{\text{molar rate of formation of product, } x_i}{\text{total molar rate of formation of products, } \sum x_i} \quad (3)$$

Gas phase products, consisting of CO and CO₂, were measured relative to a N₂ standard and reported as the %CO in the product gas, defined by Eq. 4.

$$\%CO = \frac{CO}{CO+CO_2} * 100 \quad (4)$$

3. Results

3.1 Physical properties of Pd/SiO₂ and PdSn/SiO₂ catalysts

Physical properties of the catalyst samples, including results from H₂ chemisorption and particle size analysis via electron microscopy, are summarized in Table 1. The Pd/SiO₂-H catalyst prepared by the IE method exhibited the highest H/Pd ratio of 0.80 followed by Pd/SiO₂-L (H/Pd = 0.32). Only 6.1% of the Pd was exposed in the PdSn/SiO₂-C despite utilizing the same Pd deposition method to prepare Pd/SiO₂-H. The PdSn/SiO₂-P sample mixture also exhibited a decrease in exposed Pd when the sample was reduced at 623 K in flowing H₂ prior to H₂ chemisorption (H/Pd = 0.51). No chemisorbed hydrogen was detected on Sn/SiO₂.

Figure 1 presents dark field STEM images of the fresh monometallic Pd and Sn catalysts. The STEM images for Pd/SiO₂-L and Pd/SiO₂-H show well-dispersed nanoparticles in size ranges of 2.4 ± 0.5 and 1.1 ± 0.4 nm, respectively. As for the Sn/SiO₂ sample, individual nanoparticles were not observed in STEM, but the EDS results confirmed the presence of Sn (not shown) suggesting that Sn may be dispersed as single atoms on SiO₂.²⁶ Despite depositing the Pd using a technique shown to produce well-dispersed nanoparticles,^{24,27-29} a low amount of Pd was exposed to the gas phase in the PdSn/SiO₂-C catalyst. Moreover, a variety of particle sizes was observed in STEM images, ranging from 1 nm to 100 nm (Fig. S1). Drift-corrected EDS line scans were used to characterize the large particles, defined as those in excess of 75 nm, in both the fresh and used catalyst samples. Those results, presented in Fig. S2, indicate the presence of both Pd and Sn in the fresh and used samples.

The samples were examined by X-ray diffraction and no features associated with metal particles were detected on the fresh and used monometallic Pd/SiO₂-H catalyst. Figure 2 shows the powder X-ray

diffraction patterns of fresh and used PdSn/SiO₂-C together with the positions of selected peaks from reference Pd (JCDPS 00-005-0681), Pd₃Sn₂ (JCPDS 00-007-0170), and Pd₂Sn (JCPDS 00-026-1297). In contrast to the results from monometallic Pd/SiO₂-H, distinct XRD peaks were observed with fresh and used PdSn/SiO₂-C catalysts. The fresh PdSn/SiO₂-C catalyst exhibited a broadened feature with components at 39.4°, 40.2°, and 40.7°. The feature positions are close to characteristic XRD peaks of reference Pd, Pd₃Sn₂, and Pd₂Sn. Used PdSn/SiO₂-C exhibited a weak feature at 39.4° characteristic of Pd₂Sn.

The STEM-HAADF images and results from EDS analyses of a fresh physical mixture of Pd and Sn, denoted as PdSn/SiO₂-P, can be found in the supplemental materials (Fig. S3). The EDS results of the fresh catalyst sample indicate Pd and Sn are not present on the same support particles. Clearly, the Pd nanoparticles and the Sn species reside on different silica support particles prior to being subjected to reaction conditions, including pre-reduction. The EDS analysis of used PdSn/SiO₂-P confirmed the physical migration of Sn after the catalyst was subjected to in situ pre-reduction and reaction conditions (Fig. S4 and S5). Both Pd and Sn can be found in the same regions of the used catalysts, as well as on the same support particle (Fig. 3). The 3-D STEM-EDS maps (Fig. 3) of Pd and Sn illustrate the co-location of the metals with respect to each other in the used PdSn/SiO₂-P sample. A 3-D STEM-EDS map (Fig. 4) of used PdSn/SiO₂-C, formed by IWI of Sn on Pd/SiO₂, is included for comparison.

3.2. Catalytic activity in deoxygenation of heptanoic acid

3.2.1 Particle size effect

Metal particle size is correlated to the stability of catalytic Pd nanoparticles during deoxygenation reactions of fatty acids when an excess of H₂ is present.¹¹ In this study, Pd catalysts with particles differing in size by about a factor of 2 are compared in an environment devoid of excess co-fed H₂. The conversion of heptanoic acid with time over Pd/SiO₂-L and Pd/SiO₂-H is shown in Fig. 5a. Both

catalysts achieved similar peak conversion of about 17-18% after 1.5 h on stream. The Pd/SiO₂-H catalyst maintained higher conversion after 10 h, exhibiting a 12% conversion of heptanoic acid compared to 4.2% conversion over the Pd/SiO₂-L catalyst. At the observed peak of activity, 1.5 h on stream, the Pd/SiO₂-L had a TOF of 0.0045 s⁻¹ compared to Pd/SiO₂-H, which had a TOF of 0.0027 s⁻¹. After 10 h on stream, the TOF exhibited by Pd/SiO₂-L had decreased by 71% to 0.0013 TOF s⁻¹. The TOF over Pd/SiO₂-H decreased by 33% to 0.0018 s⁻¹ after 10 h. Evidently initial rate and catalyst stability are inversely related in this system.

Product distributions characteristic of each monometallic Pd catalyst can be found in Fig. 5c and 5d. The primary liquid phase (C₆) product formed over both Pd catalysts is hexene, but more than 70% of these olefinic products are 2 and 3-hexene (i-hexene), while approximately 10% of the product is 1-hexene. Higher selectivity to 1-hexene, the direct alpha olefin product from decarbonylation of heptanoic acid, is favored at lower conversions, which is consistent with previous studies by Lopez-Ruiz et al.^{12,13} The %CO was measured at 0.5 h time on stream and after 10 h time on stream (Table 2). The total olefin selectivity (1-hexene+i-hexene) is expected to match the %CO in the gas phase products as both are a result of decarbonylation. The %CO observed at 0.5 h and after 10 h time on stream for both the Pd/SiO₂-L and Pd/SiO₂-H are consistent with the observed liquid phase products, i.e. decarbonylation was the primary reaction path over Pd.

3.3.2 Effect of Sn addition

Monometallic Sn/SiO₂ was relatively inactive in heptanoic acid conversion under the examined reaction conditions at metal loadings comparable to the Pd/SiO₂ experiments. For example, conversion of heptanoic acid after 3 h of time on stream was 0.55%, approximately 0.5% higher than the background conversion over silica. The primary product over Sn/SiO₂ was 7-tridecanone with a selectivity of 67%. Heptanal, hexadiene, hexane and 1-hexene were the other primary products with

selectivities of 9.7%, 8.4%, 7.4%, and 4.4%, respectively. The remaining 3.1% consisted of an unknown product. A complete summary of the product distribution formed over Sn/SiO₂ can be found in Fig. S6.

The addition of Sn to Pd may have improved the stability of Pd under the deoxygenation conditions utilized in this study (Fig. 6), but the conversions were not consistent between the catalysts. Most importantly, PdSn/SiO₂-C maintained relatively constant 8% conversion of heptanoic acid after the usual initial break-in period. Likewise, the physical mixture PdSn/SiO₂-P exhibited a similar level of activity and stability as the bimetallic PdSn/SiO₂-C catalyst, converting 7% of heptanoic acid after more than 10 h time on stream. An additional test involving a physical mixture of Pd/SiO₂-H and bare silica, containing the same amount of Pd/SiO₂ as PdSn/SiO₂-P and denoted as Pd/SiO₂-D, was evaluated to ensure that the activity and stability of the physical and chemical mixtures of Pd and Sn was the result of Sn and not the low TOF associated with Pd/SiO₂-H. The dilution of Pd/SiO₂-H with bare silica, Pd/SiO₂-D, did not alter the product selectivity associated with the monometallic Pd during conversion of heptanoic acid. As shown in Fig. 6a, the deactivation observed for Pd/SiO₂-D, which was tested at the same level of conversion as the Sn-promoted catalysts, confirms the positive effect of Sn on stabilizing the Pd catalysts.

The addition of Sn to a Pd catalyst significantly altered the product distribution observed over monometallic Pd during heptanoic acid conversion. The reaction over PdSn/SiO₂-C (Fig. 6b) produced 7-tridecanone, formed via decarboxylative ketonization, as a major product with a selectivity of 38% at 0.5 h time on stream. Heptanal, formed via dehydration, was also produced with a selectivity of 28% at 0.5 h time on stream. The selectivities to 1-hexene, i-hexene, hexadiene, and hexane were 3.7%, 2.3%, 1.2%, and 1.2%, respectively. An unknown product was detected at 0.5 h time on stream with a selectivity of 25%, assuming a similar response factor, but the selectivity decreased to 2% after 2 h. As the time on stream increased to 10.75 h, the selectivity to 7-tridecanone decreased to 12% and the selectivity to heptanal increased to 36%. Roughly equal amounts of 1-hexene and i-hexene were produced with

selectivities of 18% and 22 %, respectively, and hexadiene was produced with a selectivity of 5.9%. Interestingly, hexane was not produced in significant quantities after 10.75 h time on stream.

Initially, the physical mixture of PdSn/SiO₂-P (Fig. 6c) had a product distribution that was largely characteristic of Pd/SiO₂-catalyzed heptanoic acid deoxygenation. More than 80% of the initial products were consistent with a monometallic Pd/SiO₂ catalyst, with 7-tridecanone making up the balance. The product distribution changed with time on stream until the selectivity patterns of PdSn/SiO₂-P and the PdSn/SiO₂-C catalysts were nearly identical. Heptanal was the primary deoxygenated product over the PdSn/SiO₂-P catalyst with a selectivity of 42%. Internal double bond isomers of hexene comprised 14% of the products while 1-hexene was 18%. The 7-tridecanone product accounted for 15% whereas hexadiene was 9.0% of the products.

The %CO in the gas phase products observed during the conversion of heptanoic acid over the PdSn/SiO₂-C and PdSn/SiO₂-P catalysts is shown in Table 2. The %CO observed over both PdSn catalysts after 10 h on stream did not match well the selectivity to decarbonylation products. The explanation for the lower than anticipated %CO observed is unknown, but it might indicate some conversion of CO to CO₂ via the water-gas-shift reaction.

3.4 Effect of Sn proximity to Pd

To further probe the promotional effect of Sn on Pd, heptanoic acid was passed through a reactor containing a Pd/SiO₂-H section and a Sn/SiO₂ section separated by glass wool to ensure there was no direct contact between the supported catalysts. The two different catalyst bed configurations that were tested are illustrated in Fig. 7a. The configurations are designated as M₁/M₂ where M₁ was the catalyst at the bottom of the reactor and was the first to contact the heptanoic acid feed.

The general shape of the conversion curves for both configurations (Fig. 7b) is nearly identical to Pd/SiO₂-H (Fig. 5a) in which there is an increase in conversion to a maximum followed by deactivation.

When heptanoic acid contacted the Pd catalyst first (Pd/Sn), the product distribution reported in Fig. 7c resembled that from a reaction catalyzed by a monometallic Pd/SiO₂ catalyst. Most importantly, 7-tridecanone and heptanal were not observed in the reaction products.

The configuration in which the heptanoic acid contacted Sn/SiO₂ prior to Pd/SiO₂ (Sn/Pd) exhibited greater conversion of heptanoic acid compared to the Pd/Sn configuration (Fig. 7b). The greater heptanoic acid conversion when it contacts the Sn catalyst first is reflected in a new product distribution (Fig. 7d). For the Sn/Pd configuration, 7-tridecanone was formed at a selectivity of 30% after 10.75 h on stream, whereas i-hexene selectivity was only 42%. The selectivity to 1-hexene and hexane remained largely unchanged from those produced over the Pd/Sn configuration at 11 and 14%, respectively.

The percent of CO in the gas phase from each catalyst bed configuration is presented in Table 3. The %CO is largely consistent with the measured amounts of decarbonylation products versus decarboxylative ketonization product.

3.3 In situ XANES analysis

Figure 8 shows the Sn K-edge XANES spectra collected over the course of H₂ TPR for Sn/SiO₂, PdSn/SiO₂-C, and PdSn/SiO₂-P catalysts. Compared to bulk SnO₂³⁰, which has an E₀ at 29.2053 keV, all the unreduced catalyst samples present a very similar spectrum with an identical E₀ white line intensity at 298 K, indicating that the oxidation state of Sn in the samples is close to that of SnO₂. During the temperature ramp in flowing 5% H₂/He, the XANES spectrum of Sn/SiO₂ revealed a gradual decrease in the white line intensity up to 508 K (Figs. 8a and 8d), indicating a partial reduction of the supported SnO₂. Addition of Pd, i.e. in PdSn/SiO₂-C, promoted a more extensive reduction of the SnO₂ as evidenced by a more substantial decrease in the white line intensity (Figs. 8b and 8d) and likely caused by hydrogen spill-over³¹. The white line intensities associated with the physically mixed PdSn/SiO₂-P catalyst were

positioned between those of Sn/SiO₂ and PdSn/SiO₂-C (Figs. 8c and 8d).

Figure 9 presents the in situ XANES spectra for PdSn/SiO₂-C and PdSn/SiO₂-P catalysts during butyric acid conversion at 573K. The XANES spectrum of PdSn/SiO₂-P in the presence of butyric acid remained unchanged from that of pre-reduced PdSn/SiO₂-P, indicating the Sn species present under reaction conditions are likely partially reduced oxides (Fig. 9b). The lower intensity of the white line in the XANES spectrum of pre-reduced PdSn/SiO₂-C (Fig. 9a) compared to PdSn/SiO₂-P (Fig. 11b) indicates the Sn species is more reduced in PdSn/SiO₂-C. The presence of butyric acid, however, slightly increased the white line intensity of PdSn/SiO₂-C resulting in an E₀ that was very close to that of PdSn/SiO₂-P catalyst (Fig. 9b). Thus, the chemical state of the Sn in the bimetallic catalyst during reaction is similar to that of the physical mixture.

4. Discussion

4.1 Structural properties of Pd, Sn, and PdSn catalysts

The lack of XRD features associated with the monometallic catalysts is consistent with the very high dispersion of the Pd/SiO₂ and the Sn/SiO₂ samples. In contrast, XRD features were observed for both the fresh and used PdSn/SiO₂-C catalyst, as illustrated in Fig. 2. The expected Pd (111) peak at 40.1° appeared to be shifted to 39.4° for the fresh and used PdSn/SiO₂-C, which is attributed to the substitution of the larger Sn atom into the Pd lattice. Indeed, the peak at 39.4° is consistent with a Pd₂Sn alloy.³² An additional peak at 40.7° is observed in the diffraction pattern of the fresh PdSn/SiO₂-C sample, which could suggest a Pd₃Sn₂ crystal structure, which exhibits a strong diffraction peak at 41.0°. The peak at 40.7° is, however, absent in the diffraction pattern of the used PdSn/SiO₂-C catalyst.

4.2 Catalytic performance of Pd, Sn, and PdSn catalysts in deoxygenation of heptanoic acid

4.2.1 Activity of Pd catalysts

Deoxygenation of fatty acids over carbon and silica supported noble metal catalysts, including Pd, has been demonstrated to proceed via decarbonylation and decarboxylation (Schemes 1A and 1B).^{9,12,13,33} In the present study, the high selectivity to olefin products accompanied by formation of CO indicates that decarbonylation is the primary route of deoxygenation over monometallic Pd/SiO₂ catalysts under the examined reaction conditions. For example, after 10.75 h on stream, hexenes accounted for 84% of the hydrocarbon products and the %CO found in the gas phase product stream was 88% (Table 2). The other major product formed over Pd/SiO₂ was hexane, with a selectivity of 14%, which corresponds well to the %CO₂ value of 12%. Since the product selectivity exhibited by both monometallic Pd catalysts was similar, the Pd particle size between 1-2 nm did not affect the preferred reaction path.

In contrast, the particle size influenced the stability and TOF of the Pd/SiO₂ catalyst. Sun et al. observed that larger particles experienced less severe deactivation while converting octanoic acid over Pd/SiO₂ in the presence of dihydrogen.¹¹ The opposite result was observed in the current work on conversion of heptanoic acid in absence of dihydrogen. Results in Fig. 5 clearly show the catalyst with larger Pd particles (Pd/SiO₂-L) deactivating faster than the catalyst with smaller Pd particles (Pd/SiO₂-H). Smaller Pd particles may deactivate slower because they are catalyzing the reaction at a lower TOF. Lugo-José et al. showed that the TOF for hydrodeoxygenation of propanoic acid over Pd/SiO₂ remains constant when particles are between 3.0-12.4 nm, but decreases by a factor of 2-3 as the Pd particles decreased in size below 3 nm.³⁴ In the present study, lower TOF of the smaller Pd particles may decrease the rate of self-poisoning which is manifested as more stable activity of the catalyst.

4.2.2 Activity of PdSn catalysts

The physical mixture of Pd and Sn, PdSn/SiO₂-P, initially exhibited selectivity in heptanoic acid conversion that was characteristic of monometallic Pd/SiO₂-H. The change in product selectivity over the

PdSn/SiO₂-P from primarily decarbonylation (typical of monometallic Pd) to primarily dehydration, decarbonylation and decarboxylative ketonization suggests the catalyst structure changes under reaction conditions. The EDS analysis of used PdSn/SiO₂-P indicates the physical migration of Sn to the silica support particles containing Pd nanoparticles. Treatment in H₂ appears to facilitate some of the Sn migration during the pre-reduction step, as indicated by the decreased H/Pd from H₂ chemisorption results observed for the PdSn/SiO₂-P compared to the Pd/SiO₂-H. However, the change in product selectivity with time on stream suggests that a more substantial migration occurred when heptanoic acid flowed over the catalyst.

The migrating Sn species during reaction are hypothesized to be volatile tin carboxylates formed via the reaction between SnO_x species and heptanoic acid.³⁵ These tin species may decompose on Pd sites located on and within nearby silica particles or simply be deposited on the silica support.³⁵ The SnO_x species present in the fresh PdSn/SiO₂-P catalyst are extremely well dispersed as indicated by the lack of observable particles by HR-TEM. The very low heptanal formation rate observed over the Sn/Pd reactor configuration compared to that observed from the PdSn/SiO₂-P and PdSn/SiO₂-C catalysts indicates Sn species are incapable of migrating through the glass wool separating the Sn and Pd catalyst beds.

In situ XANES studies suggest that a Pd and Sn bulk alloy is not likely the active phase of the bimetallic system. Migration and redeposition of Sn in the physical mixture PdSn/SiO₂-P forms a partially reduced SnO_x that was responsible for the production of heptanal under reaction conditions. Metal oxide catalysts possessing moderate strength metal-oxygen bonds, including Fe₂O₃ and SnO₂, have been shown to be selective for dehydration of carboxylic acids in the presence of H₂ through a reverse Mars and Van Krevelen mechanism (Scheme 1D).³⁶⁻³⁸ Addition of a metal capable of hydrogen spillover, such as Pt, facilitates reduction of the metal oxide, thus promoting aldehyde formation.^{38,39} The hydrogen required to form oxygen vacancies may come from the water-gas shift reaction on Pd sites. Such a side

reaction is consistent with the observed discrepancy of %CO observed for both PdSn/SiO₂-C and PdSn/SiO₂-P.

The product distribution from heptanoic acid conversion over bimetallic PdSn/SiO₂-C changed throughout the course of the 10.75 h run. The XRD patterns for the fresh and used bimetallic catalyst indicate a change in crystal structure of the metal particles after exposure to reaction conditions. Nevertheless, the in situ XANES study of PdSn/SiO₂-C during butyric acid conversion confirms partially reduced SnO_x species are similar to those present on the physical mixture. Carboxylic acids containing two α -hydrogens, such as heptanoic acid, will undergo decarboxylative ketonization on metal oxide surfaces that do not contain a prevalence of oxygen vacancies.^{37,38} Evidently, the initial state of PdSn/SiO₂-C favors production of 7-tridecanone (Fig. 6b) which decreases at later times on stream.

4.2.3 Stability of PdSn catalysts

The SnO_x species surrounding Pd sites in both physically-mixed and chemically-mixed PdSn/SiO₂ catalysts appear to promote the stability of the catalyst. Prior work demonstrated SnO_x can supply oxygen-containing species that oxidatively remove CH₃CO and CO adsorbed on adjacent noble metal sites.^{40,41} In addition, Pd-promoted SnO_x/SiO₂ has been reported to exhibit higher rates of CO oxidation compared to unpromoted SnO_x/SiO₂.¹⁷ Thus, removal of product CO and unreacted heptanoic acid might be facilitated by the presence of Sn. Although an alloy phase was detected in the chemically mixed PdSn/SiO₂-C, we suspect it resides in the few large bimetallic particles that would likely be irrelevant in the reaction.

5. Conclusion

The reactivity of silica-supported Pd, Sn, and PdSn bimetallic catalysts was evaluated in the conversion of heptanoic acid. Whereas monometallic Pd converted heptanoic acid primarily through

decarbonylation, addition of Sn altered the reaction network to include dehydration and decarboxylative ketonization. In addition to altering the product distribution, addition of Sn to Pd improved the stability of the catalyst. Physically-mixed PdSn/SiO₂-P and chemically-mixed PdSn/SiO₂-C catalysts exhibited similar rates and selectivities after long times on stream, suggesting the final state of the catalyst is similar in both cases. Characterization of a used catalyst revealed a physical migration of Sn to Pd during reaction over the physical mixture. Analysis of Sn K-edge XANES suggests that the chemical state of Sn on the PdSn catalysts is a SnO_x species that forms under reaction conditions.

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List of Tables

Table 1: Physical properties of the Pd, Sn, and PdSn catalysts

Catalyst	Hydrogen chemisorption (mmol H ₂ /g of catalyst)	H/Pd ratio	Particle diameter ^a (nm)	Surface-weighted avg. diameter ^b (nm)	Nominal metal loading (wt %)	
					Pd	Sn
Pd/SiO ₂ -L	0.076	0.32	3.1	2.4 ± 0.5	5	-
Pd/SiO ₂ -H	0.19	0.80	1.3	1.1 ± 0.4	5	-
Sn/SiO ₂	0	-	-	-	-	5.6
PdSn/SiO ₂ -C	0.0072	0.061	-	-	2.5	2.8
PdSn/SiO ₂ -P	0.059	0.51	-	-	2.5	2.8

^aResult estimated from 1/(H/Pd).

^bResult calculated from $\sum d^3 / \sum d^2$ where diameter (d) is measured using STEM images.

Table 2: The %CO during heptanoic acid conversion at 573 K

Catalyst	%CO	
	TOS = 0.50 h ^a	TOS = 10.75 h ^a
Pd/SiO ₂ -L	68	88 ^b
Pd/SiO ₂ -H	71	88 ^c
PdSn/SiO ₂ -C	8	50
PdSn/SiO ₂ -P	60	39

^aTOS represents time on stream

^bResult taken at 10 h time on stream.

^cResult taken at 11 h time on stream.

Table 3: The %CO during heptanoic acid conversion at 573 K over two separated catalyst beds

Catalyst configuration	%CO	
	TOS = 0.50 h ^a	TOS = 10.75 h ^a
Sn/Pd	64	54
Pd/Sn	76	94

^aTOS represents time on stream

List Figures

A) Decarbonylation

B) Decarboxylation

C) Decarboxylative ketonization

D) Dehydration

Scheme 1: Deoxygenation of heptanoic acid via A) decarbonylation, B) decarboxylation, C) decarboxylative ketonization, and D) dehydration.

Figure 1: Dark field STEM images of fresh a) Pd/SiO₂-L, b) Pd/SiO₂-H, and c) Sn/SiO₂

Figure 2: XRD pattern for fresh and used PdSn/SiO₂-C from a) 15°-90° and b) zoomed in to 30°-50°. Used catalyst was tested for heptanoic acid conversion at 573 K and 0.1 MPa for 10.75 h.

Figure 3: 3-D STEM-EDS map of used PdSn/SiO₂-P: a) Pd-L map; b) Sn-L map. Used catalyst was tested for heptanoic acid conversion at 573 K and 0.1 MPa for 10.75 h.

Figure 4: 3-D STEM-EDS map of used PdSn/SiO₂-C: a) Pd-L map; b) Sn-L map. Used catalyst was tested for heptanoic acid conversion at 573 K and 0.1 MPa for 10.75 h.

Figure 5: a) Conversion and b) TOF of heptanoic acid deoxygenation at 573 K and 0.1 MPa over Pd/SiO₂-L and Pd/SiO₂-H. Product selectivities are shown for c) Pd/SiO₂-L and d) Pd/SiO₂-H.

a)

b)

Figure 6: a) Conversion of heptanoic acid at 573 K and 0.1 MPa over Pd/SiO₂-H, Pd/SiO₂-D, PdSn/SiO₂-C, and PdSn/SiO₂-P and selectivity to deoxygenation products over b) PdSn/SiO₂-C and c) PdSn/SiO₂-P.

Figure 7: a) Configuration of two different catalyst beds in the reactor. Catalyst beds were separated by glass wool. Configurations are designated as M_1/M_2 where M_1 is the first catalyst to contact the reagent. b) Conversion of heptanoic acid at 573 K and 0.1 MPa over separated beds of Pd/SiO₂-H and Sn/SiO₂. c) Product selectivity during reaction over Pd/Sn configuration. d) Product selectivity over Sn/Pd configuration.

Figure 8: In situ Sn K-edge XANES spectra during temperature programmed reduction in 5% H₂ of a) Sn/SiO₂, b) PdSn/SiO₂-C, c) PdSn/SiO₂-P, and d) comparison of white line intensities. Spectra are offset for clarity.

a)

b)

Figure 9: In situ Sn K-edge XANES of a) PdSn/SiO₂-C and b) PdSn/SiO₂-P during the conversion of butanoic acid. Spectra for “calcined catalyst” are associated with fresh, unreduced catalyst in flowing N₂. Spectra for “in situ reduction” are associated with the catalyst after reduction in situ at 623 K for 30 min under 100 cm³ min⁻¹ 5% H₂/He. Spectra for “reaction conditions” are associated with the catalyst at 573 K after 150 min exposure to butanoic acid in N₂.