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1. Introduction

Deoxygenation refers to a broad class of chemical reactions involving the removal of oxygen from organic compounds that can be accomplished by reactions such as dehydration, decarbonylation and decarboxylation. Carboxylic acids found in vegetable oils and animal fats can be readily converted to fuels and chemicals by decarbonylation and decarboxylation reactions. For example, linear organic acids are converted to linear alkenes and linear alkanes by decarbonylation and decarboxylation, respectively, as shown for the reaction of heptanoic acid in Scheme 1. Recent work on decarbonylation and decarboxylation of carboxylic acids over transition metal catalysts is often performed in the presence of dihydrogen to inhibit catalyst deactivation, but the reactions are highly selective towards the production of paraffins because of the rapid hydrogenation of any alkenes formed in the process.^{1,2} Terminal alkenes formed by decarbonylation are appealing organic materials because of their application in the polymer industry. Therefore, an effective catalyst for decarbonylation prevents both hydrogenation of product α -olefin as well as the double bond isomerization to form internal olefins.

Relatively little has been reported on the conversion of fatty acids to olefins, with generally poor results being presented in



Scheme 1 Decarbonylation and decarboxylation of heptanoic acid.

terms of catalyst efficiency and selectivity towards terminal olefin formation in the product.^{1,3} In 1982, Maier et al. studied the decarboxylation of carboxylic acids for production of fuellike hydrocarbons.⁴ In their work, they showed that supported Pd and Ni catalysts were highly selective towards deoxygenation products. In 2006, Murzin and coworkers studied several other supported metals such as Ru, Pt, Ir, Os, and Rh, and they concluded that the most promising of the transition metals are Pd and Pt, which achieved more than 90% selectivity towards alkane and alkene production when the metals were supported on carbon.¹ Nickel has also been extensively studied for deoxygenation of fatty acids and triglycerides, but is not an attractive metal because it favors alkane production and cracking.^{1,5,6} Furthermore, Maier et al. showed that a variety of fatty acids can be converted over Ni and Pd catalysts *via* decarboxylation, however, the use of H_2 in the reaction was essential.4

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Decarbonylation of heptanoic acid over carbon-supported platinum nanoparticles

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The decarbonylation and decarboxylation of heptanoic acid over carbon-supported Pt nanoparticles were studied in a continuous flow fixed bed reactor at 573 K and 37 bar for liquid-phase operation and 1 bar for gas-phase operation. Under liquid-phase conditions, the TOF over Pt supported on Norit carbon was 0.0052 s⁻¹ and independent of Pt loading. At very low conversions, approaching zero, the product selectivity was consistent with decarbonylation as the primary reaction, producing mostly hexenes and CO. As conversion increased from 1% to 5% at 37 bar, substantial amounts of hexane and CO₂ were observed, presumably from secondary side reactions such as water-gas shift (WGS) and hydrogenation instead of direct decarboxylation. The terminal olefin was observed with high selectivity (57%) only during gas-phase operation (1 bar) which facilitated transport of the olefin away from the Pt that also catalyzed double bond isomerization. Some sintering of the Pt metal particles during reaction of heptanoic acid was observed by X-ray diffraction analysis of the spent catalyst. Catalyst regeneration studies were performed over spent catalyst but they failed to restore any catalytic activity.

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Scheme 2 Ketonization of heptanoic acid.



Scheme 3 Hydrogenation of 1-hexene.

A recent study showed that ketonization can play an important role in upgrading fatty acids into fine chemicals or fuels.⁷ This reaction involves the coupling of two carboxylic acids to produce a symmetrical ketone with the simultaneous removal of oxygen in the form of CO_2 and H_2O , as depicted in Scheme 2. Gaertner *et al.*⁸ theorized that ketonization might be an intermediate step in the deoxygenation reaction and, in the presence of a transition metal, the ketone could further convert to olefins (mostly α -olefins) and CO. The ketonization reaction is also referred to as ketonic decarboxylation.

As mentioned above, hydrogenation is an important side reaction that can also take place over supported metal catalysts (see Scheme 3). Because hydrogenation of α -olefins forms less valuable paraffins, sources of hydrogen in the reaction need to be minimized. Some studies on decarboxylation and decarbonylation include H₂ not only to maximize the selectivity towards the formation of paraffins (typically for fuel components), but also to influence the deoxygenation rate.^{9,10} Snåre *et al.* showed that reaction under low H₂ conditions formed coke.¹⁰ Olefins can also be formed from the decarboxylation of unsaturated fatty acids that had been dehydrogenated earlier in the reactor.⁹

In this study, we studied systematically the decarbonylation and decarboxylation of heptanoic acid over a wide variety of carbon-supported Pt catalysts in a steady-state, fixed bed flow reactor to elucidate the reaction path and evaluate the turnover frequency of the reaction. In particular, the influences of Pt dispersion, Pt loading, carbon support and reaction phase on the conversion of heptanoic acid and selectivity to various products were explored.

2. Experimental methods

2.1. Catalyst synthesis

The catalysts were prepared by an incipient wetness impregnation method using aqueous solutions of tetraammineplatinum(II) nitrate, $(NH_3)_4Pt(NO_3)_2$ (Sigma Aldrich) to obtain 1, 3, 5, and 10 wt% Pt loadings. Norit activated carbon (ROX 0.9), SiC (SICAT β -SiC), and Vulcan carbon (VXC72R) were used as supports for the metal particles. Prior to impregnation, Norit C and SiC support particles were crushed and sieved between 180 μ m and 425 μ m. Vulcan C powder was used as received. After impregnation of the desired Pt precursor solution, the catalyst was dried in air at 393 K overnight. The dried solids were then reduced in H₂ (GT&S 99.999%) flowing at 100 cm³ min⁻¹. The temperature of reduction was increased at 5 K min⁻¹ from room temperature to the desired value, which ranged from 623 to 873 K, and held isothermally for 3 h. The catalyst was then cooled, exposed to air, and stored in a vial.

2.2. Dihydrogen chemisorption

The metal dispersion was measured by H_2 chemisorption performed on a Micromeritics ASAP 2020 adsorption system. The catalyst was evacuated at 573 K for 10 h under vacuum followed by heating to 623 K at a rate of 5 K min⁻¹ after which it was reduced with flowing H_2 (GT&S 99.999%) at 623 K for 2 h.

Following reduction, the catalyst sample was evacuated at 623 K and cooled to 308 K in vacuum. The chemisorption of H_2 was performed at 308 K over the pressure range of 40 to 450 Torr. The amount of metal on the surface was evaluated by the total amount of H_2 adsorbed extrapolated to zero pressure, assuming a stoichiometric relationship between H_2 to metal $(H_2: Pt)$ of 1:2 (*i.e.* H/Pt = 1).

2.3. Dinitrogen physisorption

The specific surface area and pore size were measured by N_2 physisorption using a Micromeritics ASAP 2020. The samples were evacuated for 180 min at 373 K prior to the N_2 physisorption, after which adsorption isotherms were measured at 77 K. The Brunauer–Emmett–Teller (BET) and the Barrett–Joyner–Halenda (BJH) methods were used to determine the specific surface area and the pore size, respectively.

2.4. X-ray diffraction

Powder X-ray diffraction (XRD) analysis was carried out on a X'Pert Pro MPD with monochromatic Cu Kα-radiation (λ = 1.54056 Å) using a step size of 1/4° and a time step of 1 s. Diffraction angles were measured from $2\theta = 20^{\circ}$ to 100°. The Scherrer equation was used to estimate the particle size as described in Patterson *et al.*¹¹

2.5. Electron microscopy

Transmission electron microscopy (TEM) was performed on a FEI Titan operated at 300 keV in EFTEM mode. Catalyst samples were deposited on a SPI lacey-carbon coated Cu grid after being dispersed in methanol.¹² Fresh (after catalyst synthesis) and spent (after exposure to reaction conditions) catalyst samples were imaged to determine the effect of reaction conditions on particle morphology. The spent samples were recovered from the reactor, washed with 25 mL of methanol and sonicated in a methanol solution for 30 min to remove reactant and products from the surface of the catalyst. After

sonication, the solids were recovered by filtration and dried overnight in air at 400 K.

2.6. Catalytic conversion of heptanoic acid

The decarbonylation/decarboxylation of fatty acids can be a challenging reaction, mainly because of low reaction rates and rapid catalyst deactivation.² Furthermore, saturated fatty acids with more than 9 carbons in the aliphatic chain have a high melting point. This physical property makes operation in a continuous mode particularly challenging since the entire pumping system as well as the reactor must be heated. In this study, heptanoic acid was selected as the reactant because it is a liquid at room temperature, therefore eliminating the need to pre-heat the lines and the pumping system.

Decarbonylation/decarboxylation reactions are often performed in a solvent with H_2 simultaneously fed to the reactor to extend catalyst life. Under these conditions, the fatty acid could be hydrogenated before deoxygenation, leading to the formation of alcohols and other products, which can react with the acid substrate to form esters.^{2–4,7–9,13,14} To avoid undesirable side reactions, neither solvent nor H_2 was cofed with the heptanoic acid. Dodecane was used as an internal standard because it has a similar boiling point to heptanoic acid and is thermally stable. The amount of dodecane was minimized (5 wt%) to avoid hydrogen transfer from it to the products.⁹

The main organic products from converting heptanoic acid were expected to be 6 carbon hydrocarbons, hexane, 1, 2, and 3-hexene, and the ketonization product 7-dihexyl ketone (a symmetrical ketone). These compounds were therefore monitored by gas chromatography.

The catalytic decarbonylation/decarboxylation of heptanoic acid (Sigma Aldrich 99.0%) was performed in a 1/4" OD $\times 8"$ length \times 0.035" wall thickness stainless steel fixed bed reactor. After loading the catalyst in the reactor, the system was first flushed for 30 min with 100 cm³ min⁻¹ of N₂ (GT&S 99.999%) at 40 bar to remove any dioxygen from the system and to perform a leak test. Then, the temperature was increased to the desired reduction temperature, 623–873 K, under 100 cm³ min^{-1} of N₂ at 5 K min⁻¹ at 1 bar. The temperature was held isothermally for 2 h as the catalyst was reduced in H₂ (GT&S 99.999%) flowing at 100 cm³ min⁻¹ at atmospheric pressure. The reactor was finally cooled to the reaction temperature, 573 K, and pressurized to 37 bar in 100 $\text{cm}^3 \text{ min}^{-1}$ of N₂ (GT&S 99.999%). The feed mixture was composed of 95 wt% heptanoic acid (Sigma Aldrich 99.00%) and 5 wt% dodecane (Sigma Aldrich anhydrous 99.00%). The feed was pumped into the reactor containing 0.25 g of catalyst using a syringe pump (ISCO 500D) operating at different liquid flow rates (0.005, 0.01, or 0.05 $\text{cm}^3 \text{min}^{-1}$). The acid feed passed through a heated zone before entering the catalytic reactor. The reactor was operated in an upflow mode because gases were generated in the reaction. Fig. 1 shows a schematic of the reactor system.

The outlet of the reactor was connected to a condenser, maintained at room temperature, and samples of the liquid and gas products were collected approximately every 150 min.





Fig. 1 Schematic diagram of reactor system. TC represents a thermocouple, GC represents a gas chromatograph, PG represents a pressure gauge, and PC represents a back pressure regulator.

The liquid sample was analyzed by a gas chromatograph (Agilent 7890A) equipped with a ZB-FFAP column (length 45 m \times 0.538 mm) and a flame ionization detector. The presence of dodecane as an internal standard allowed for quantification of the products.

The product gas was continuously removed from the condenser by an N₂ (GT&S 99.999%) purge gas, which was fed to an on-line gas chromatograph (HP 5890 Series II) equipped with a packed column, ShinCarbon ST 80/100, and a thermal conductivity detector (TCD) for detection of N₂, CO, CO₂, and light hydrocarbons (if any). The N₂ purge gas was also used to maintain pressure in the system and was the internal standard for GC analysis.

A series of control experiments was performed to determine the background conversion of the system at our typical reaction conditions (573 K, 37 or 1 bar, and 0.01 cm³ min⁻¹ of liquid feed composed of 95 wt% heptanoic acid and 5 wt% dodecane). In the absence of catalyst, no conversion of heptanoic acid was observed. However, when Norit carbon and Vulcan carbon supports were used, a background conversion of 2–3% was detected. No conversion was observed over SiC.

2.7. Turnover frequency and selectivity calculations

The turnover frequency (TOF) was defined by Boudart as the number of revolutions of the catalytic cycle per unit time.¹⁵ In this work the TOF was calculated as the rate of formation of the products referred to the number of surface Pt atoms. The main components in the liquid products were hexane (C6), 1-hexene (α-C6), 2 and 3-hexenes (i-hexenes, i-C6), 7-tridecanone (ketone), and minor amounts of heavier unknown products (which accounted for $\approx 3\%$ of the total detected liquid product). The TOF was therefore calculated as [(rate of production (mol s⁻¹) of C6 + α -C6 + i-C6 + 2× moles of ketone + others)/(mol of surface Pt counted by H₂ chemisorption)]. The major gas products observed were CO and CO2. The product selectivity was defined as the moles of a product formed divided by the total moles of all identified products present in the same phase (liquid or gas), *i.e.* selectivity of 1-hexene [(rate of α -C6)/(rate of all C6 products + moles of 7-tridecanone +

moles of unknowns)] and selectivity of CO [(rate of CO)/(rate of CO + rate of CO_2)]. Selectivities of liquid and gas products were calculated independently.

The TOF associated with the Pt was based on measured rates after subtracting the background conversion from the support and normalized by the dispersion of Pt evaluated on a freshly prepared catalyst.

2.8. Mass transfer limitations

The mass transfer characteristics were estimated using the Weisz–Prater criterion for internal transport limitations (Φ_{I}), eqn (1),

$$\Phi_{\rm I} = \frac{r_{\rm obs} R_{\rm p}^2 \rho_{\rm p}}{D_{\rm EA} C_{\rm AS}} < 1 \tag{1}$$

and the analogous expression for external transport limitations ($\Phi_{\rm E}$), eqn (2),

$$\Phi_{\rm E} = \frac{r_{\rm obs} R_{\rm p} \rho_{\rm p}}{k_{\rm A} C_{\rm AB}} < 0.15 \tag{2}$$

assuming first order reaction.¹⁶ In eqn (1) and (2), $r_{\rm obs}$ is the observed rate, $R_{\rm p}$ is the radius of the support particle, $\rho_{\rm p}$ is the density of the catalyst pellet, $D_{\rm EA}$ is the effective diffusivity, $k_{\rm A}$ is the external mass transfer coefficient, $C_{\rm AS}$ is the surface concentration, and $C_{\rm AB}$ is the bulk concentration of heptanoic acid.^{16,17}

The effective diffusivity $(D_{\rm EA})$ was estimated using a porosity $(\varepsilon_{\rm P})$ of 0.5 and a tortuosity (τ) of 3 as recommended in Davis and Davis.¹⁷ The self-diffusion coefficient $(D_{\rm AA})$ for heptanoic acid was calculated using the Stokes–Einstein equation for analysis of the liquid-phase and using gas kinetic theory for analysis of the gas-phase reaction. Because the average Pt particle size was ≈ 2 nm or greater, it was assumed for this analysis that the size of the pore in which the catalytic reaction takes place is at least 2 nm, which was used to calculate the Knudsen diffusivity $(D_{\rm KA})$ for the gas-phase operation. The external mass transfer coefficient $(k_{\rm A})$ was obtained using a mass transfer correlation for fluid–solid interface for packed bed reactors obtained from Cussler.¹⁸

Using the highest observed rates, $\Phi_{\rm I}$ was calculated to be much less than 1 for the liquid and gas phase reactions (0.005 and 0.012, respectively) and $\Phi_{\rm E}$ was much less than 0.15 for the liquid and gas phase reactions (0.004 and 0.001, respectively) for a catalyst particle size of 425 µm. The criteria suggest that the system was not mass transfer limited with respect to the reactant.

Results and discussion

3.1. Effect of carbonaceous support

Carbon is a widely used support for transition metals in deoxygenation reactions because of its high surface area $(700-1500 \text{ m}^2 \text{ g}^{-1})$ and relative inertness.^{1,2,19-24} Carbon supports are available in different particle sizes, surface areas, and pore size distributions. Most carbon supports are difficult to pelletize, which may account for why so many of the earlier studies in the field were performed in batch systems. Operation of a fixed bed reactor system with a fine powder can develop a very large pressure drop across the catalyst bed. Therefore, we chose to explore some of the pelletized carbons as supports for Pt nanoparticles.

Three different carbonaceous supports were tested in this study, each having very different physical properties. Norit carbon is a high surface area support that can be purchased in pellet form, which can be easily crushed to the desired particle size. However, it has many small pores that might influence the transport rates of products out of the pellets and therefore affect the side reactions. Vulcan carbon is nonporous, but has a much smaller surface area than Norit carbon. Furthermore, the as-received Vulcan carbon could not be easily pelletized. Preliminary tests of Vulcan carbon powder in our fixed bed reactor revealed a very large pressure drop when we tried to pump liquid reactant through the bed. Therefore, Vulcan carbon was only used as a support for Pt in experiments with gaseous heptanoic acid. Silicon carbide is a macroporous support that was obtained in pellet form. However, it has a much lower surface area than Norit carbon.

Catalysts composed of 5 wt% Pt supported on the various carbon supports were characterized using N_2 physisorption, H_2 chemisorption, and XRD, and the results are summarized in Table 1. While a high Pt dispersion of 31% was obtained on Norit carbon, very large Pt particles were formed on Vulcan carbon and SiC. The diffraction peaks in Fig. 2 observed at about 39.5°, 45.5°, 57°, and 79.5° are attributed to the (111), (200), (220), and (311) reflections of Pt.²⁵ Analysis of the peak width by the Scherrer equation gave an average Pt crystallite size of 21 and 40 nm for Pt supported on Vulcan C and SiC, respectively. The lack of a Pt diffraction pattern associated with Pt/Norit C was consistent with the high metal dispersion revealed by H_2 chemisorption.

The three catalysts were tested under the same reaction conditions (573 K, 0.25 g of catalyst, and a flow rate of 0.01 cm³ min⁻¹) and their performance is summarized in Table 2.

The most obvious conclusion from Table 2 is the highest conversion of heptanoic acid over Pt/Norit C, presumably because of the highest metal dispersion. The results in Table 2 also show an effect of the reaction phase on the product selectivity. For Pt/Norit C and Pt/SiC, the selectivity towards the formation of α -olefin was increased in gas-phase reaction

Table 1 Summary of the characterization results for 5 wt% Pt on different supports

Support	Dispersion (%)	Surface area $(m^2 g^{-1})$	Pore size (nm)	Pt particle size (nm)
Norit carbon	31 ^{<i>a</i>}	1428	N.D. ^b	3.7 ^{<i>a</i>}
SiC	_	217 26	20	40^{c}

^{*a*} Result estimated from H₂ chemisorption. ^{*b*} Not determined, both micropores and mesopores are present on this sample. ^{*c*} Result obtained using XRD patterns and Scherrer equation.



Fig. 2 Comparison of the XRD patterns of 5 wt% Pt supported on Norit carbon, Vulcan carbon and SiC reduced at 623 K under 100 cm³ min⁻¹ of H₂ at a heating rate of 5 K min⁻¹. \square Represents features of SiC support. The patterns were offset for clarity.

at 1 bar compared to the liquid-phase reaction at 37 bar. On Pt/Norit C, internal olefins were the majority product at both liquid-phase and gas-phase conditions. However, the product distribution on Pt/SiC shifted from mostly paraffin (hexane) to mostly ketone after moving from the liquid-phase conditions into the gas-phase.

Given the lack of success with preparing highly dispersed Pt on Vulcan C and SiC after reduction at 623 K, and the unfavorable product distributions on Pt/Vulcan C and Pt/SiC, we decided to focus our efforts on studying the behavior of Pt/ Norit C.

3.2. Effect of reduction temperature

Simakova *et al.*²⁶ previously showed that Pd catalysts with different but high metal dispersions can exhibit different activities and product distributions. However, those catalysts with high dispersions approached similar activity after prolonged reaction times.²⁶

To obtain different Pt metal dispersions on 3 wt% Pt/Norit C, we reduced the same catalyst at four different temperatures (625, 673, 773 and 873 K) and tested them in the reaction of

 Table 3
 Result of the characterization of 3 wt% Pt/Norit C reduced at four different temperatures

- 1 - 1	Metal	Pt particle size (1	nm)	Surface
Reduction temperature (K)	dispersion (%)	Chemisorption	TEM	$(m^2 g^{-1})$
623	49	2.3	1.9 ± 0.2	1477
673	21	5.3	2.1 ± 0.5	1348
773	13	8.9	2.5 ± 0.8	1495
873	13	8.4	$\textbf{3.1} \pm \textbf{1.0}$	1374

heptanoic acid. Table 3 summarizes the results of the catalyst characterization by chemisorption, physisorption and electron microscopy.

Although the dihydrogen uptake decreased on the samples reduced at elevated temperatures, electron microscopy revealed very little growth of the small particles (from 2 to 3 nm). These contrasting findings could be the result of some Pt migrating outside of the Norit C pores to form large particles on the external surface. It should be noted that a wider Pt particle size distribution was observed by microscopy, which is consistent with Pt migration on the sample. Fig. 3 shows the images of the catalysts obtained by TEM.

Conversion of heptanoic acid and product distribution over the catalyst reduced at different temperatures were monitored for 35 h, and the results are presented in Fig. 4 and 5. The catalytic activity and product distribution of the four catalysts did not reach steady state until about 15 to 20 h of reaction. Because of this induction period, the cause of which is unknown, the results in all of the subsequent tables are reported after at least 15 to 20 h of reaction.

As expected, increasing the reduction temperature decreased the Pt dispersion, which negatively affected the conversion. However, the TOF associated with the four catalysts was relatively constant at 0.0052 s⁻¹ (Table 4). The constancy of the TOF suggests that the system was not mass transfer limited since the Koros–Nowak (or Madon–Boudart) criterion is obeyed at this one reaction temperature, which is consistent with the conclusion from mass transfer criteria discussed earlier.²⁷

Table 4 shows that the product distributions in the liquid (olefins and paraffin) and gas (CO and CO_2) over the four catalysts were different. Although this finding differs from the literature, it could be a result of the different conversion levels

Table 2	Effect of support	on the reaction	of heptanoic acid	l over Pt nanoparticles ^a
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			Selectivity (%	6)			
Support	Pressure (bar)	Conversion (%)	α-Olefin	i-Olefin	Paraffin	Ketone	Others
Norit carbon	37	10.3	5.65	61.0	28.4	0.6	4.3
	1	11.1	26.4	55.6	15.3	3.4	0.4
Vulcan carbon	1	3.5	14.1	64.7	18.5	0.2	2.6
SiC	37	1.6	2.5	19.9	54.7	3.5	19.5
	1	0.5	22.7	0.0	18.6	58.7	0.0

^{*a*} The reaction was run at 573 K, 37 bar for liquid-phase experiments and 1 bar for gas-phase experiments, with 0.25 g of catalyst and a flow rate of 0.01 cm³ min⁻¹ composed of 95 wt% heptanoic acid and 5 wt% dodecane.



Fig. 3 TEM images of fresh 3 wt% Pt/Norit C catalyst reduced at four different temperatures. (A) was reduced at 623 K, (B) was reduced at 673 K, (C) was reduced at 773 K, and (D) was reduced at 873 K.

achieved by each catalyst.²⁶ Furthermore, the selectivity towards the formation of α -olefin was very low and was most likely due to rapid double bond isomerization over the Pt at the reaction temperature.

3.3. Effect of metal loading

Given the non-uniformity of the Pt particle size distribution formed by varying the reduction rate, we decided to test the performance of heptanoic acid conversion over catalysts with different Pt loadings but reduced at the same temperature. Therefore, four catalysts with different metal loadings of 1, 3, 5, and 10 wt% Pt were synthesized and tested at two different reaction temperatures. The results from characterization and reaction testing are summarized in Table 5 and Fig. 6.



Fig. 4 Effect of reduction temperature (\bullet represents 623 K, \bullet represents 673 K, \blacktriangle represents 773 K, and \blacksquare represents 873 K) on heptanoic acid conversion over 3 wt% Pt/Norit C. The reactions conditions were 573 K, 37 bar, and 0.01 cm³ min⁻¹ of feed composed of 95 wt% heptanoic acid and 5 wt% dodecane.

As expected, the conversion of heptanoic acid increased with the amount of surface Pt in the reactor. The TOF at 553 and 573 K was constant at each temperature over the four different metal loadings tested with an average value of 0.0022 s⁻¹ and 0.0052 s⁻¹, respectively. Furthermore, the TOF obtained at 573 K matched the one obtained over 3 wt% Pt/Norit C reduced at different temperatures (Table 4).

Increasing the Pt loading did not considerably increase the Pt particle size but instead increased the number of particles per unit of area, as shown by the TEM images in Fig. 7. The average Pt particle size obtained by TEM was relatively constant at a value of about 2 nm for all the samples, while the value estimated by H₂ chemisorption varied between 2.3 and 4.0 nm (Table 5). Again, this difference might be due to some large Pt particles on the external surface of the pellets that were not observed by microscopy but were accounted for by H₂ chemisorption.



Fig. 5 Effect of reduction temperature (\bullet represents 623 K, \bullet represents 673 K, \blacktriangle represents 773 K, and \blacksquare represents 873 K) on the olefin (left) and CO (right) selectivity over time during the conversion of heptanoic acid over 3 wt% Pt/Norit C. The reactions conditions were 573 K, 37 bar, and 0.01 cm³ min⁻¹ of feed composed of 95 wt% heptanoic acid and 5 wt% dodecane. Olefin selectivity is relative to liquid products only and CO selectivity is relative to CO + CO₂.

Table 4 Effect of metal dispersion on the decarbonylation/decarboxylation of heptanoic acid over 3 wt% Pt/Norit C^a

				Product se	electivity (%)				
Reduction temperature (K)	Dispersion (%)	$TOF(s^{-1})$	Conversion ^{b} (%)	α-Olefin	i-Olefins	Liquid Paraffin	Ketone	Others	Gas CO
623	49	0.0052	9.1	5.2	63.2	27.7	1.2	2.7	57.7
673	21	0.0051	3.8	5.0	62.9	28.2	1.4	2.5	69.1
873	13	0.0051	2.4	4.8 5.0	54.7	34.0	4.0	2.3	55.4

^{*a*} The reactions conditions were 573 K, 37 bar, 0.01 cm³ min⁻¹ of feed composed of 95 wt% heptanoic acid and 5 wt% dodecane. Results were recorded after 20 h of reaction. ^{*b*} Background conversion has been removed.

Table 3 Effect of Filloautha of hebianoic acture action over Filmonic C at 333 N and 373 N	Table 5	Effect of Pt loading on	heptanoic acid reaction ove	r Pt/Norit C at 553 K and 573 K
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		Pt particle size (nm	l)	Conversio	$\operatorname{pn}^{b}(\%)$	$\operatorname{TOF}^{b}(\operatorname{s}^{-1})$	
Loading (wt% Pt/C)	Dispersion (%)	Chemisorption	TEM	553 K	573 K	553 K	573 K
1.0	28	4.0	1.8 ± 0.4	0.7	1.7	0.0022	0.0052
3.0	49	2.3	1.9 ± 0.2	_	9.1	_	0.0052
5.0	31	3.7	1.9 ± 0.3	4.4	8.2	0.0024	0.0045
10.0	39	2.9	2.1 ± 0.5	10.1	24.3	0.0021	0.0051

^{*a*} The catalysts were tested at 37 bar and 0.01 cm³ min⁻¹ of feed composed of 95 wt% heptanoic acid and 5 wt% dodecane. Results were recorded after 20 h of reaction. ^{*b*} Background conversion has been removed.



Fig. 6 Effect of Pt weight loading supported on Norit C on product selectivity and conversion at 573 K, 37 bar, and $0.01 \text{ cm}^3 \text{ min}^{-1}$ of feed composed of 95 wt% heptanoic acid and 5 wt% dodecane. The product selectivity (%) is represented with color bars and can be read on the left axis. \Box Represents 1-hexene, \boxtimes represents 2 and 3-hexenes, \blacksquare represents hexane, \blacksquare represents 7-tridecanone, and \blacksquare represents the unknown products. The black squares represent conversion (%) and can be read on the right axis. These results were recorded after 20 h of reaction.



Fig. 7 TEM images of fresh Pt/Norit C catalysts reduced at identical conditions but with four different Pt loadings. (A) has 1 wt% loading, (B) has 3 wt% loading, (C) has 5 wt% loading, and (D) has 10 wt% loading.

As shown in Fig. 6, the product selectivity changed as the metal loading and therefore the conversion increased. For example, the overall selectivity towards the formation of olefins decreased at higher conversion; interestingly the relatively low selectivity of α -olefin relative to all olefins (1, 2, and 3-hexenes) remained constant (Fig. 6).

Due to a lack of reported TOF values for the decarbonylation/decarboxylation reactions over Pt catalysts, we compared our TOF values to those reported for Pd. In general, the TOF obtained with Pt in this study was lower than the TOF reported in the literature for Pd. For example, TOF values over Pd ranged from 0.01 to 0.96 s⁻¹ for batch reaction at 573 K^{22-24,28} and from 0.027 to 0.004 s⁻¹ for fixed-bed operation at 543 K.^{2,13} As mentioned in the Experimental methods section, Norit C revealed a low level of background conversion ($\approx 2\%$) at our reaction conditions (573 K, and 0.01 cm³ min⁻¹ of feed), which contributed significantly to the observed conversion at low Pt loadings or low Pt dispersions. If the background conversion were not accounted for properly, the TOF for Pt would be artificially inflated. Likewise, for Pd catalysts with low loadings or low dispersions, it is possible that some background conversion on the support could contribute to the high TOF reported in the literature.^{22,26} Furthermore, most of the experiments with Pd involved co-feeding H₂ and diluting the fatty acid with long chain hydrocarbons, which have been reported to enhance the TOF and the stability of the catalyst.^{9,10}

3.4. Effect of flow rate

To minimize the impact of support activity on the results, we chose to study a 10 wt% Pt/Norit C catalyst at various flow rates of heptanoic acid to explore the influence of conversion on the product distribution. The feed flow rate was varied from 0.005 to 0.05 cm³ min⁻¹ over a period of 120 h (\approx 2200 turnovers) to obtain a range of conversion values. Fig. 8 shows the relationship between space time and conversion, which was fairly linear at low conversion. At higher conversions, however, the catalyst appeared to be less active than expected, which might be evidence for inhibition by product CO on the Pt sites. The conversion at very short space time was reproduced after 120 h of reaction, confirming that a long term deactivation process was not significant during the course of this particular experiment. If the Pt metal nanoparticles sintered under reaction conditions, particle growth must have occurred during the initial induction period.



Fig. 8 Dependence of conversion of heptanoic acid at different flow rates over 10 wt% Pt/Norit C at 573 K and 37 bar. These results were recorded after 20 h of reaction. The W/F was calculated as the weight of catalyst used divided by the mass flow rate.



Fig. 9 Dependence of decarbonylation product selectivity on conversion over 10 wt% Pt/Norit C at 573 K and 37 bar. \blacksquare Represents the selectivity to decarbonylation products, olefins, in the liquid product. \blacklozenge Represents the selectivity to decarbonylation product, CO, in the gas product. \blacktriangle Represents the selectivity to α -olefins in the liquid product. These results were recorded after 20 h of reaction.

Fig. 9 shows a very strong correlation of the product selectivity to conversion. Extrapolation of the product selectivity for gaseous products (CO + CO₂) to zero conversion indicates 80% of the gas product is CO. Likewise, extrapolation of the liquid-phase products to zero conversion results in 80% selectivity to olefins. Evidently, the initial reaction of heptanoic acid under these conditions is mainly decarbonylation. The very low selectivity to α -olefins was the result of rapid isomerization of the double bond in 1-hexene over Pt to form 2 and 3 hexenes.

With increasing conversion, the selectivity for CO decreased more extensively than the selectivity for olefins, suggesting there is a side reaction that converts CO into CO₂. A likely side reaction is the water-gas shift (WGS) reaction shown in Scheme 4, which is believed to play an important role in the decarbonylation/decarboxylation reactions, not only for converting CO into CO₂, but for providing a source of H₂ that can hydrogenate the olefins into paraffin.^{23,24} In contrast, Lestari et al. theorized that CO is actually formed from CO₂ in the reverse water-gas shift reaction, rather than by direct decarbonylation reaction of fatty acids.²⁹ Our results in Fig. 9 clearly support the idea that decarbonylation was the primary reaction on Pt metal nanoparticles under our experimental conditions. The fact that the fraction of olefins in the liquid products exceeded the fraction of CO in the gaseous products at increasing conversions (Fig. 9) suggests that the WGS reaction occurs more readily than the hydrogenation of olefins using H₂ produced by WGS. Fig. 9 also shows that selectivity of a-olefins (1-hexene) in the liquid product was always less than about 10%,

 $CO + H_2O \equiv CO_2 + H_2$

Scheme 4 Water-gas shift (WGS) reaction.

even at very low conversions. Evidently, the double bond isomerization of 1-hexene to 2 and 3-hexenes was rapid over Pt catalysts in the liquid-phase conversion of heptanoic acid at 573 K.

3.5. Effect of pressure

Previous studies showed that the formation rate of alkene did not match that of CO.^{2,22} Our results clearly show that reactions of the primary products, α -olefin, CO (and presumably H₂O), proceed at rates that are quite rapid. The formation of CO₂ and H₂ *via* the water–gas shift reaction, which is then followed by hydrogenation of olefin to paraffin, might account for the product distribution at higher conversion. Although the conversion of heptanoic acid was not mass transfer limited with respect to the acid, it is possible that rapid conversion of the primary products in the catalyst pores might be limited by mass transfer rates out of the catalyst particles. To increase the effective diffusivity and external mass transfer coefficient of the molecules, we performed exactly the same reaction experiments at 1 bar pressure, which allows the major products and heptanoic acid to remain in the gas phase.

Fig. 10 compares the performance of Pt/Norit C with different metal loadings and system pressures. For operation with liquid-phase reactant (37 bar), the main products at high conversions (>20%) were hexane and CO₂. At lower conversions, mostly olefins were produced, although they were mainly 2 and 3 hexenes formed from double bond isomerization of 1-hexene. When the reaction was run at low pressure (1 bar) resulting in gas-phase conditions in the reactor, the selectivity towards the formation of α -olefin was higher than that in the liquid phase. Moreover, higher metal loadings in the catalyst pores facilitated subsequent conversion of the

 α -olefin to the internal olefins, even at low pressure. Fig. 10 also shows that lowering the conversion by increasing the reactant flow rate improved selectivity to α -olefin, which is expected when α -olefin is a primary product of decarbonylation.

It should be noted that the conversion of heptanoic acid over the three different Pt catalysts did not correlate with the surface Pt when operated in the gas-phase, which contrasts the direct relation observed in the liquid-phase, as reported in Fig. 10 and Table 5. We attribute the observed behavior of Pt catalysts in gas-phase operation to significant deactivation, which is discussed in the next section.

3.6. Catalyst deactivation

Catalyst deactivation during the deoxygenation of carboxylic acids has been widely reported in the literature. Snåre *et al.*¹⁰ and Mäki-Arvela *et al.*¹³ suggested that deactivation originated from poisoning of the metal by the reactants, products (especially CO), and coking. Furthermore, Simakova *et al.* reported that deactivating aromatics are formed in reactions performed under H₂-scarce conditions.³⁰ The initial concentration of carboxylic acid is also proposed to influence catalyst deactivation. Mäki-Arvela *et al.* observed that deactivation was more extensive with higher initial concentration of carboxylic acid.¹³

Ping *et al.* imaged Pd nanoparticles supported on silica with TEM before and after reaction.³¹ The catalyst did not show a significant increase in metal particle size after reaction indicating negligible metal sintering occurred. Since most of the catalyst activity was regained after hot extraction with solvent and subsequent reduction in H_2 at 573 K, the authors



Fig. 10 Effect of reaction pressure and feed flow rate on catalyst activity and product distribution over Pt/Norit C with different loadings of Pt during the conversion of heptanoic acid at 573 K. The feed composition was 95 wt% heptanoic acid and 5 wt% dodecane. The color bars can be read on the left axis and represents the product distribution. \Box Represents 1-hexene, \boxtimes represents 2–3-hexenes, \blacksquare represents hexane, \blacksquare represents 7-tridecanone, and \blacksquare represents the unknown products. The black squares represent conversion (%) and can be read on the right axis. These results were recorded after 20 h of reaction. (A) was run in liquid-phase (37 bar) conditions and flow rate of 0.01 cm³ min⁻¹. (B) was run in gas-phase (1 bar) conditions and a flow rate of 0.05 cm³ min⁻¹.



Fig. 11 Effect of deactivation on catalyst activity and product distribution over 10 wt% Pt/Norit C during the conversion of heptanoic acid at 573 K and a feed flow rate of $0.01 \text{ cm}^3 \text{ min}^{-1}$ composed of 95 wt% heptanoic acid and 5 wt% dodecane. The bars with patterns represents the product distribution and can be read on the left axis. \Box Represents 1-hexene, \boxtimes represents 2–3-hexenes, \blacksquare represents hexane, \blacksquare represents 7-tridecanone, and \blacksquare represents the unknown products. The black squares represent conversion (%) and can be read on the right axis. These results were recorded after 20 h of reaction.

concluded that the observed deactivation resulted from deposition of organic molecules onto the active sites. 31

Fig. 11 summarized catalyst performance after several changes in reaction conditions to study the deactivation phenomenon. Although our studies revealed stable operation of Pt/Norit C up to 120 h of operation with the liquid-phase reactant, we observed significant deactivation during gasphase operation at 1 bar. For this series of experiments, the catalyst was assumed to be at steady state after prolonged liquid-phase reaction. At this point, the pressure was lowered to 1 bar to begin operation in the gas phase. Although the conversion decreased after the phase change, catalyst deactivation continued to lower conversion with time. After 40 h of gasphase operation, the catalyst deactivated to half its activity at the time of the phase change. The pressure was then increased to return to liquid-phase operation. After 20 h of steady state operation in liquid-phase conditions, the catalyst activity remained low, indicating the liquid-phase flow was unable to recover the original activity.

The deactivated catalyst was finally exposed to flowing heptanoic acid at 350 K at 1 bar for 24 h to remove possible products from the surface. The reactor was then flushed with N_2 and heated at 5 K min⁻¹ to reaction temperature. Since the catalyst activity was not regained by this treatment, the catalyst was also re-reduced in flowing H_2 at 623 K and 1 bar for 4 h, but again the activity was not recovered. A mild oxidation treatment of the catalyst in air at 623 K and 1 bar for 4 h followed by a rereduction in flowing H_2 at 623 K and 1 bar for 4 h also did not re-activated the catalyst. Clearly, the mode of deactivation was not easily reversed by standard regeneration methods.

Fig. 12 shows high magnification TEM images of three Pt/ Norit C catalysts with different weight loadings after 80 h of reaction in gas-phase operation conditions, and they did not reveal substantial particle growth compared to the fresh



Fig. 12 TEM images of spent Pt/Norit C catalysts. The catalysts were prepared by IWI and reduced with H₂ at 623 K at a heating rate of 5 K min⁻¹. (A) represents a spent sample of 1 wt% Pt, (B) represents a spent sample of 5 wt% Pt, and (C) represent a spent sample of 10 wt% Pt. The spent samples were first run in liquid-phase operation until steady-state operation and then they were run in gas-phase operation until deactivation. At that point in time, the spent samples were recovered from the reactor and treated as described in the Experimental methods section. The spent catalysts were collected after a total of 80 h under reaction conditions.

samples shown in Fig. 7. In contrast, XRD patterns of the catalyst before and after reaction presented in Fig. 13 suggested the presence of some large Pt particles on the spent catalysts. The resulting average particle size of the spent catalyst was



Fig. 13 Comparison of the XRD patterns of Norit C support, fresh 10 wt% Pt/Norit C after reduction, and spent 10 wt% Pt/Norit C after reaction. The spent sample was first run in liquid-phase operation until steady-state operation and then it was run in gas-phase operation until deactivation. At that point, the spent sample was recovered from the reactor and treated as described in the Experimental methods section. The spent catalyst was collected after a total of 80 h under reaction conditions. The patterns were offset for clarity.

estimated with the Scherrer equation to be 19 nm. The migration and sintering of Pt would explain why the various attempts at catalyst regeneration were unsuccessful. The sintering of Pt particles was not observed in Fig. 12 because the images were associated with very thin areas of the sample to obtain good contrast for imaging. We speculate that the large Pt particles reside outside the small pores of the carbon support. Indeed, the small Pt particles of 2 to 3 nm observed in Fig. 12 probably reside inside the highly porous structure Norit C which likely inhibited particle growth inside the pores.

Fig. 14 presents a schematic diagram of our working hypothesis for deactivation of the Pt particles during reaction. What is apparently unknown at this point is why gas-phase operation facilitates deactivation compared to liquid-phase operation. We hypothesize that some organic species are strongly absorbed on the Pt particles after gas-phase operation.

Although metal sintering observed by XRD might occur very early during the reaction, which might account for the lower



4. Conclusions

Platinum nanoparticles were supported on Norit carbon, Vulcan carbon and silicon carbide, characterized by chemisorption, X-ray diffraction and electron microscopy, and evaluated in the conversion of heptanoic acid at 573 K. Results from characterization and reactivity confirmed that highly dispersed Pt was formed in Norit carbon (dispersion $\approx 49\%$) after a mild reduction treatment at 623 K. Similar treatment of Pt/Vulcan carbon and Pt/SiC resulted in the formation of much larger particles of Pt. Variations of Pt dispersion, Pt loading and reactor space time were used to explore the influence of conversion on product distribution during heptanoic acid reaction over Pt/Norit C. In summary, decarbonylation of heptanoic acid was the primary reaction to produce olefin, CO and water. Rapid conversion of α-olefin to internal olefin was observed in liquid-phase operation, even at low conversion. Higher selectivity to α -olefin product was achieved by operation in the gas phase, presumably because of the greater rate of mass transfer of product molecules out of the catalyst pores. Although various criteria indicated the rate of heptanoic acid conversion was not limited by mass transfer, subsequent reactions of the products could be. Higher conversion of heptanoic acid in liquid-phase operation also was accompanied by sequential conversion of CO to CO₂, presumably via water-gas shift reaction. In addition, hydrogenation of olefin was observed at higher conversion as expected from H₂ generated by the WGS reaction. A summary of the reaction network observed here is provided in Fig. 15.





Fig. 14 Schematic depiction of working hypothesis for catalyst sintering.

Fig. 15 Reaction network for the decarbonylation/decarboxylation of heptanoic acid over supported Pt at low conversion levels.

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