

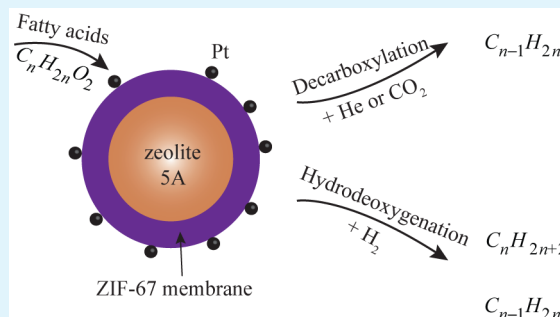
Deoxygenation of Palmitic and Lauric Acids over Pt/ZIF-67 Membrane/Zeolite 5A Bead Catalysts

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ABSTRACT: The deoxygenation of palmitic and lauric acids over 0.5 wt % Pt/ZIF-67 membrane/zeolite 5A bead catalysts is demonstrated. Almost complete conversion (% deoxygenation of $\geq 95\%$) of these two fatty acids was observed over both fresh and recycled catalyst after a 2 h reaction time. The catalysts displayed high selectivity to pentadecane and undecane via decarboxylation reaction pathway even at low 0.5 wt % Pt loading. Selectivity to pentadecane and undecane as high as $\sim 92\%$ and $\sim 94\%$ was observed under CO_2 atmosphere when palmitic and lauric acids were used respectively as reactants. Depending on the reaction gas atmosphere, two distinctive reaction pathways were observed: decarboxylation and hydrodeoxygenation. Specifically, it was found that decarboxylation reaction pathway was more favorable in the presence of helium and CO_2 , while hydrodeoxygenation pathway strongly competed against the decarboxylation pathway when hydrogen was employed during the deoxygenation reactions. Esters were identified as the key reaction intermediates leading to decarboxylation and hydrodeoxygenation pathways.

KEYWORDS: decarboxylation, palmitic acid, lauric acid, hydrocarbons, reaction pathway



1. INTRODUCTION

Lipid biomass, derived from vegetal oils, is a low cost, abundant renewable feedstock that can be used to produce liquid fuel hydrocarbons by removing oxygen from fatty acid chains in complex fatty acid ester mixtures. These liquid hydrocarbons are typically employed in the synthesis of valuable petrochemicals, fuels, and lubricants. Vegetable oils are key raw materials to produce renewable fuels. Vegetable oils can contain as high as 71% of oleic acid.¹ Besides oleic acid, other fatty acids, including palmitic acid and lauric acid, are present in vegetable oils in considerable amounts. For example, palmitic acid composition in several vegetable oils can be as high as 20%.¹ Lauric acid comprises $\sim 50\%$ of the total fatty acid composition in several oils including coconut, laurel, and palm.²

The key reaction to convert fatty acids to liquid hydrocarbons is catalytic deoxygenation.^{3–6} The catalytic deoxygenation of fatty acids employing different heterogeneous catalysts is well documented. The deoxygenation of fatty acids and their derivatives can occur through three main different reaction pathways, including decarboxylation, decarbonylation, and hydrodeoxygenation which depend on the reaction conditions and employed catalysts. Typically, conventional hydrosulfurization catalysts, such as Ni–Mo and Co–Mo catalysts, are selective for the hydrodeoxygenation route, while the noble metal supported catalysts, especially Pd and Pt supported catalysts, are more favorable for decarboxylation and/or decarbonylation route.^{7–9} Typically, a high supply of hydrogen input is needed for the hydrodeoxygenation reaction. Decarboxylation and decarbonylation reactions may or may not

require hydrogen and therefore are cheaper routes to produce liquid hydrocarbons from lipid biomass sources.

Hybrids comprising metal–organic frameworks (MOFs) and other structures are emerging as novel materials with interesting catalytic, gas adsorption, and optical properties.^{10–14}

By combination of these two, the hybrids can be promising in various aspects like enhanced mechanical and chemical stability and unique gas adsorption behavior. Hupp and co-workers reported the formation of layer-structured MOF/metal films as hybrid metal–organic framework devices, and these structures behaved as gas and vapor sensors.¹¹ Farha and co-workers synthesized Pt@ZIF-8 composites for the regioselective hydrogenation process that displayed higher selectivity as compared to Pt/C.¹² Duan and co-workers successfully prepared gold-ZIF-8 shell structure hybrid via epitaxial growth or coalescence.¹³ These authors found that these composites exhibited superior photocatalytic properties for oxidation of benzyl alcohol.

Previously, our group documented a novel catalytic system consisting of Pt supported on zeolite 5A covered with ZIF-67 membrane.^{15,16} In these reports, we demonstrated the catalytic performance of these hybrids for the decarboxylation of oleic acid to heptadecane. Oleic acid deoxygenation has been widely studied over several catalysts, such as Pt supported on carbon,¹⁷ SiO_2 ,¹⁸ CeO_2 ,¹⁹ SAPO-34, DNL-6, RHO and hydrotalcite,²⁰ SAPO-11 and chloride Al_2O_3 ,²¹ Pd/C,²² activated carbon,²³

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Table 1. Product Distribution for the Deoxygenation of Palmitic Acid over Pt/ZIF-67 Membrane/Zeolite 5A Catalysts

		hydrocarbon product distribution (%)				
temp (°C)	gas atmosphere	hexadecane	pentadecane	tetradecane	tridecane	dodecane
280	H ₂	34.89 (40.51)	62.64 (55.86)	0.16 (0.18)	0.15 (0.14)	0.61 (1.06)
320	H ₂	23.55 (31.70)	62.84 (58.53)	0.73 (0.38)	0.74 (0.35)	1.28 (0.84)
320	helium	1.13 (1.67)	89.51 (83.93)	1.50 (2.36)	1.46 (1.71)	1.38 (1.67)
320	CO ₂	0.69 (1.33)	91.67 (88.02)	1.18 (1.78)	1.27 (1.44)	0.69 (0.88)

		hydrocarbon product distribution (%)					
temp (°C)	gas atmosphere	undecane	decane	nonane	octane	heptane	unknown
280	H ₂	0.97 (1.51)	0.12 (0.10)	0.12 (0.09)	0.11 (0.08)	0.07 (0.06)	0.16 (0.41)
320	H ₂	1.78 (1.19)	1.13 (0.50)	1.14 (0.49)	1.02 (0.46)	0.74 (0.32)	5.05 (5.24)
320	helium	1.61 (3.91)	0.93 (0.75)	0.75 (0.64)	0.63 (0.49)	0.29 (0.35)	0.81 (2.52)
320	CO ₂	2.25 (3.35)	0.78 (0.79)	0.51 (0.44)	0.52 (0.40)	0.20 (0.10)	0.24 (1.47)

molybdenum nitrate, tungsten nitrate, tungsten nitride, platinum nitride, palladium nitride, and vanadium nitride supported on γ -Al₂O₃,²⁴ hydrotalcite,²⁵ Sn-containing layered double hydroxide,²⁶ supported iron nanoparticle,²⁷ Ni/MgO-Al₂O₃,²⁸ H₃PO₄/Al₂O₃,²⁹ natural aluminosilicate as well as nanosized titanium, magnesium, zirconium, and cerium oxide.³⁰ However, the deoxygenation of saturated fatty acids including palmitic and lauric acids has been less studied. Herein, we report the deoxygenation of palmitic and lauric acids over Pt/ZIF-67 membrane/zeolite 5A catalysts. Decarboxylation and hydrodeoxygenation were the two main observed pathways, which were highly dependent on the prevailing reaction gas atmosphere.

2. EXPERIMENTAL SECTION

2.1. Preparation and Characterization of Catalysts. In a typical synthesis, Pt/ZIF-67 membrane/zeolite 5A catalysts were synthesized as follows. Two solutions were prepared. The first solution consisted of 0.45 g of cobalt nitrate hexahydrate (Sigma-Aldrich, ACS reagent $\geq 98\%$) dissolved in 3 mL of deionized water. The second solution consisted of 5.5 g of 2-methylimidazole (Sigma-Aldrich, 99%) dissolved in 20 mL of deionized water. Both solutions were stirred at room temperature for 6 h. After this, the solution was transferred into a 45 mL Teflon-lined stainless steel autoclave containing 5 g of zeolite 5A beads. The autoclave was treated at 150 °C for 6 h. The resultant layered 5A beads were stored at 100 °C overnight. A second layer of ZIF-67 was applied following the methodology described above. Then Pt at 0.5 wt % was incorporated in the ZIF-67/5A beads via conventional wet impregnation method. Specifically, tetraammine-platinum nitrate (Sigma-Aldrich, 99.995% trace metal basis) was dissolved in deionized water, followed by its impregnation on the ZIF-67/5A beads. Finally, the catalysts were dried overnight at 100 °C and calcined at 400 °C for 5 h. The resultant catalysts were characterized by X-ray diffraction, field emission scanning electron microscopy, and nitrogen adsorption. XRD patterns were collected on a Kristalloflex800 from Siemens at 25 mA and 30 kV with Cu K α radiation. Prior to the measurements, the samples were pestled into powder. Field emission electron microscopy images were collected on JEOL ISM-7000F using a field emission gun and an accelerating voltage of 5 kV. Nitrogen BET surface areas were obtained in a ASAP 2020 at 77 K using liquid nitrogen as coolant. Before the gas measurements, all catalysts were degassed at 180 °C for 6 h.

2.2. Reaction Procedures. Palmitic acid (98%, Kic Chemicals, Inc.) and lauric acid (99%, Kic Chemicals, Inc.) were used as the model saturated fatty acid molecules. Prior to the reaction, all catalysts were heated in a conventional oven at 150 °C for 3 h. The reactions were carried out in a 100 mL stainless steel, high pressure batch reactor (Parr model 4560). The model molecule and the catalyst were loaded into the reactor at mass ratio of 1:1. Before the reaction, the reactor was flushed by flowing with the desired gas (H₂, CO₂, or He) to remove stagnant air. Then, the pressure was increased to 20 bar.

The reactor was then heated to the desired reaction temperature under constant stirring rate. The reaction temperature was kept constant during the reaction time. When the reaction was completed, the reactor was quenched down to room temperature immediately using an ice bath. Finally, the catalyst was separated from the product and was washed with hexane and methanol 3 times each (first with hexane). To remove the carbonaceous species formed during reaction, the washed catalyst was treated at 300 °C for 12 h. The recycled catalysts were also characterized by the same techniques as those used for fresh catalysts.

2.3. Product Analysis. The liquid products were analyzed with a gas chromatograph (GC, 6980N) equipped with a HP-5 MS column (with dimensions of 30 m \times 250 μ m \times 0.25 μ m) and a 5973N MSD detector. Prior to the GC analysis, the liquid products were silylated with *N,O*-bis(trimethyl)trifluoroacetamide, BSTFA (Sigma-Aldrich, $\geq 99.0\%$), and kept at 60 °C for 1 h. After that, 0.2 μ L of the liquid product was injected into the GC column (250 °C, 10.52 psi) with a split ratio 100:1. The employed carrier gas was helium (flow rate 1.0 mL/min). The following conditions on the gas chromatograph were used during the analysis: 100 °C for 5 min, 300 °C for 2 min (1 °C/min). The catalytic conversion of the fatty acid was calculated from the reduction in the number of fatty acid carboxylic acid groups.^{15,16,31,32} The concentration of remaining carboxylic acid groups in the product was quantified with the acid number (ASTMD974). The acid number was quantified employing the mass of KOH in milligrams that is required to neutralize 1 g of chemical substance. To evaluate the acid number, a known amount of sample was dissolved in a mixture of ethanol and petroleum ether, then titrated with a solution of 0.1 N NaOH. Phenolphthalein was used as a color indicator.

The acid number was calculated with the following equation:

$$\text{acid number} = 56.1 \frac{NV}{W}$$

where $N = 0.1$ (N), V = volume of NaOH consumed (mL), and W = mass of the sample (g).

The deoxygenation % was calculated using the acid number of fatty acid and acid number of the product using the following relation:

$$\begin{aligned} \text{\% deoxygenation} \\ = \frac{\text{acid number of fatty acid} - \text{acid number of the product}}{\text{acid number of fatty acid}} \times 100 \end{aligned}$$

Selected product samples were analyzed by FTIR spectroscopy. FTIR spectra were obtained with Thermo Electron Nicolet 4700 instrument.

3. RESULTS AND DISCUSSION

Due to their high thermal and chemical stability, zeolite 5A beads were chosen as catalytic support. Furthermore, as compared to powders, beads are easier to recycle and can be fully recovered and therefore are more amenable for potential scale-up. ZIF-67 membrane was chosen because it promotes

Table 2. Product Distribution for the Deoxygenation of Lauric Acid over Pt/ZIF-67 Membrane/Zeolite 5A catalysts

temp (°C)	gas atmosphere	hydrocarbon product distribution (%)						
		dodecane	undecane	decane	nonane	octane	heptane	unknown
280	H ₂	40.60 (43.83)	58.18 (54.90)	0.38 (0.38)	0.19 (0.21)	0.12 (0.13)	0.08 (0.10)	0.45 (0.45)
320	H ₂	34.74 (36.88)	59.79 (56.62)	0.67 (0.46)	0.49 (0.30)	0.40 (0.21)	0.33 (0.13)	3.58 (5.4)
320	helium	3.83 (3.92)	88.69 (84.39)	0.89 (1.96)	0.82 (1.64)	0.42 (1.10)	0.27 (1.19)	5.08 (5.8)
320	CO ₂	1.76 (2.17)	93.52 (90.06)	0.84 (0.88)	0.78 (0.85)	0.62 (0.69)	0.66 (0.50)	1.82 (4.85)

better Pt dispersion and decreases Pt leaching, improving the catalyst activity and stability.^{15,16} Pt particles are the catalytic active species in the studied reaction. The catalytic results of deoxygenation of palmitic acid and lauric acid at different temperatures and gas atmospheres over 0.5 wt % Pt/ZIF-67 membrane/zeolite 5A bead catalysts are summarized in Table 1 and Table 2, respectively. For both tables, numbers in parentheses refer to the product distribution of the recycled catalysts.

The recycled catalysts displayed very similar catalytic performance as compared to the fresh catalysts, indicating chemical stability of the catalysts. Specifically, for the deoxygenation of palmitic acid (Table 1) it was observed that at 320 °C for the recycled catalysts the pentadecane selectivity slightly decreased. The lower decrease in selectivity was observed for the reaction carried out in CO₂ (91.6% for the fresh catalyst and ~88% for the recycled catalysts, corresponding to only a ~3.5% decrease in selectivity). For reaction carried out in H₂ and helium the decrease in pentadecane selectivity was in the range ~4.5–7%. For the deoxygenation of lauric acid (Table 2) the same trend was observed. Recycled catalysts in the presence of CO₂ experienced only a decrease in undecane selectivity of ~3.5%, while the recycled catalysts in the presence of H₂ and helium displayed a decrease in selectivity in the range ~4–4.5%. Previously, we demonstrated for the deoxygenation of oleic acid that the presence of CO₂ helps to remove carbon generated and deposited at the catalysts surface during the reaction.¹⁶ In principle this keeps cleaner the catalyst surface, leading to a minimum decrease in selectivity. The conversion of the two fatty acids for both fresh and recycled catalysts was almost complete (% deoxygenation of ~95%). EDX analysis indicated that there was negligible Pt leaching for the recycled catalysts. This is in good agreement with the minimum loss in catalytic activity observed for the recycled catalysts. XRD characterization of the catalysts (Figure 1) confirmed that the crystalline structure of zeolite 5A was preserved after Pt deposition, after the incorporation of ZIF-67 membrane, and after one time recycling after deoxygenation reaction, suggesting high structural stability of all catalysts. As shown in Tables 1 and 2 for both saturated fatty acids, when He and CO₂ were supplied during reaction, decarboxylation was the main reaction pathway resulting in high pentadecane and undecane selectivities. On the other hand, when H₂ was supplied during the reaction, mainly decarboxylation products (pentadecane and undecane) and hydrodeoxygenation products (hexadecane and dodecane) were observed.

Figure 2 shows representative SEM images of fresh and recycled (under H₂, He, and CO₂ atmospheres) 0.5 wt % Pt/ZIF-67 membrane/zeolite 5A bead catalyst. These images show continuous ZIF-67 membranes of ~230–270 μm thickness. The regular and consistent ZIF-67 thickness observed for the fresh and recycled catalysts indicates good mechanical stability. In our previous report we demonstrated that the use of microporous ZIF-67 crystalline layers helps to improve the

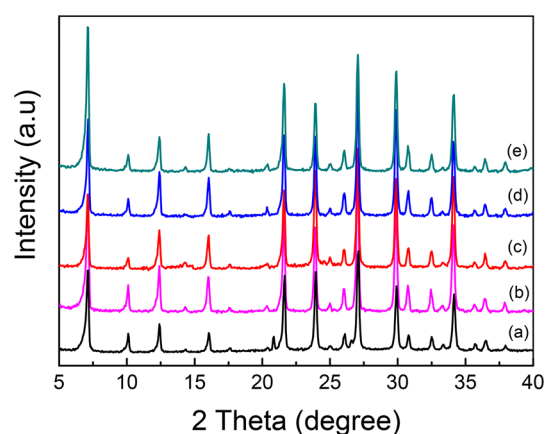


Figure 1. XRD patterns of (a) zeolite 5A, (b) fresh catalyst, (c) recycled catalyst–H₂, (d) recycled catalyst–He, and (e) recycled catalyst–CO₂.

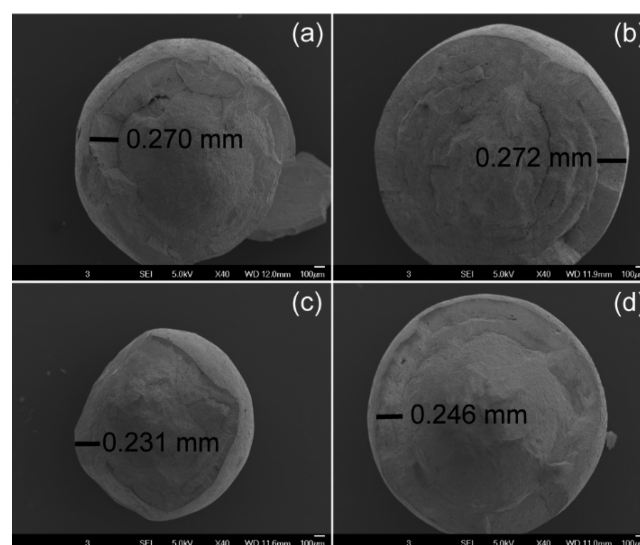


Figure 2. Representative SEM images of (a) fresh catalyst, (b) recycled catalyst–H₂, (c) recycled catalyst–He, and (d) recycled catalyst–CO₂.

stability of the resultant catalysts.¹⁵ The BET surface areas of the recycled catalysts slightly decreased (450–464 m²/g) as compared to the fresh catalysts (470 m²/g) suggesting that the catalysts can be regenerated completely after reaction. The contribution in surface area of the ZIF-67 membrane is minimum since the % weight of ZIF-67 in the hybrid catalyst is less than 10%. Therefore, the main contribution on surface area of the hybrid catalysts is from the zeolite 5A bead. In addition, the incorporation of Pt in the hybrid catalyst decreases its surface area.

The surface area of the hybrid catalyst increases as the thickness of the ZIF-67 layer increases. Specifically, we have

found BET surface areas of 470, 545, and 615 m²/g for hybrid catalysts having ZIF-67 thicknesses of 250, 300, and 360 μm, respectively.

Figure 3 shows the product distribution for the deoxygenation of palmitic acid in the presence of H₂ at two reaction

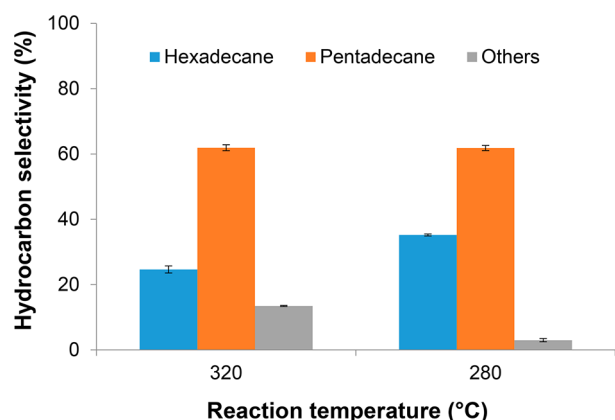


Figure 3. Effect of temperature on hydrocarbon selectivity for deoxygenation reaction of palmitic acid. Reaction conditions were the following: catalyst to fatty acid mass ratio = 1:1, H₂ atmosphere, pressure = 20 bar, time = 2 h. Error bars indicate average of two separate catalytic tests.

temperatures. Clear liquid products were obtained at reaction temperatures 320 and 280 °C. The resultant products were long chain hydrocarbons hexadecane and pentadecane and short chain hydrocarbons C₇–C₁₄, denoted as “others”. The selectivity to long chain hydrocarbons slightly increased with decreasing temperature. Furthermore, the catalytic data shown in Figure 3 indicate that the selectivity to short chain hydrocarbons increased at higher reaction temperature, suggesting cracking of hydrocarbon products.

Figure 4 shows that when lauric acid was used as reactant in the presence of H₂, the observed products were long chain hydrocarbons dodecane and undecane and short chain hydrocarbons C₇–C₁₀ denoted as “others”. Similar to the reaction in which palmitic acid was used as reactant, for lauric acid, the selectivity to long chain hydrocarbons was slightly

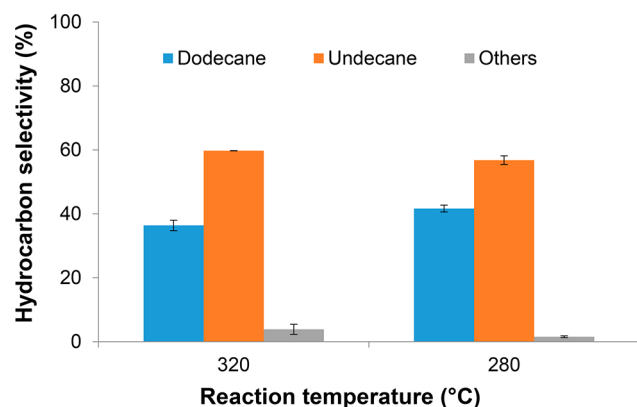


Figure 4. Effect of temperature on hydrocarbon selectivity for deoxygenation reaction of lauric acid. Reaction conditions were the following: catalyst to fatty acid mass ratio = 1:1, H₂ atmosphere, pressure = 20 bar, time = 2 h. Error bars indicate average of two separate catalytic tests.

higher when the reaction temperature was 280 °C, while the selectivity for short chain hydrocarbons was higher at 320 °C.

We studied the effect of three distinctive reaction gas atmospheres: hydrogen (reducing) to helium (inert) and CO₂ (oxidant) for the deoxygenation of palmitic and lauric acids. The main observed products for the deoxygenation of palmitic and lauric acids over Pt/ZIF-67 membrane/zeolite 5A catalysts were pentadecane and undecane, respectively. Figure 5

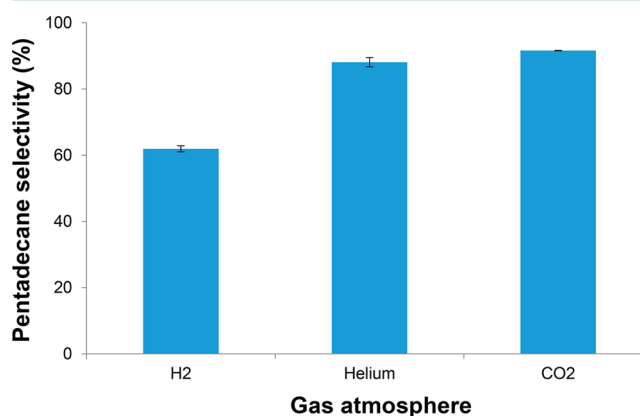


Figure 5. Effect of gas atmosphere on the selectivity to pentadecane. Reaction conditions were the following: catalyst to palmitic acid mass ratio = 1:1, temperature = 320 °C, pressure = 20 bar, time = 2 h. Error bars indicate average of two separate catalytic tests.

summarizes these results for the deoxygenation of palmitic acid. In the presence of He and CO₂ pentadecane selectivities of ~90% and 92% were observed respectively, indicating that decarboxylation was the dominant reaction pathway. On the other hand, when H₂ was used as reaction gas, pentadecane selectivity decreased to ~63%. Interestingly, hexadecane selectivity under these conditions was ~24%. These results indicate a competition between decarboxylation (pentadecane preferred) vs hydrodeoxygenation (hexadecane preferred) pathways.

As shown in Figure 6, a similar reaction pathway trend was observed when lauric acid was used as the reactant. Specifically, in the presence of He and CO₂, undecane selectivity of ~89% and 94% was observed respectively, suggesting decarboxylation as the dominant reaction pathway. When H₂ was used as

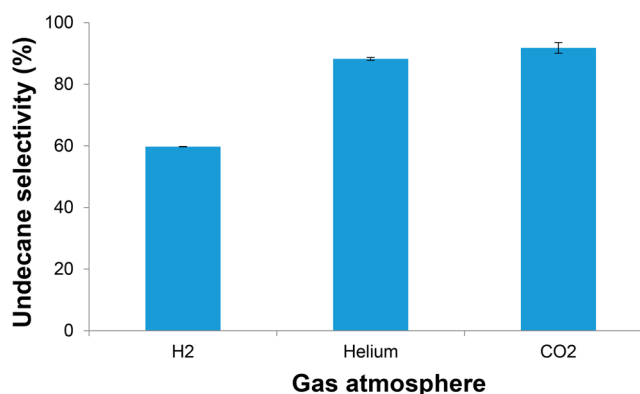


Figure 6. Effect of gas atmosphere on the selectivity to undecane. Reaction conditions were the following: catalyst to lauric acid mass ratio = 1:1, temperature = 320 °C, pressure = 20 bar, time = 2 h. Error bars indicate average of two separate catalytic tests.

reaction gas, the undecane selectivity decreased to ~60% and dodecane selectivity increased to >30%. These results indicate again a strong competition between decarboxylation products (undecane) vs hydrodeoxygenation products (dodecane).

The effect of gas environment on the selectivity of hydrocarbons for the deoxygenation of several fatty acids is well documented.^{33–38} It has been reported that supported noble metal catalysts such as Pt/C and Pd/C favor the direct decarboxylation and decarbonylation of fatty acids to produce hydrocarbons with one carbon less than the original source, even under inert atmospheres.³⁶ With hydrogen input, the reaction pathway becomes more complicated, and hydrodeoxygenation can take place.^{35,37} Under rich hydrogen atmosphere the hydrogenation of carboxylic acids (R-COOH) takes place rapidly and transforms the fatty acids into the corresponding aldehydes (R-CHO) at the beginning of the reaction, then followed by decarbonylation to produce hydrocarbons with one carbon number less and CO or further hydrogenation to alcohol.³⁷ The further hydrogenation of alcohol can produce hydrocarbons with the same carbon number as the starting fatty acid.³⁷ Therefore, the ratio of $C_nH_{2n+2}/C_{n-1}H_{2n}$ products is an indication of the hydrogenation ability of the catalysts.³⁸ In our case, the hydrogenation of palmitic acid to hexadecane and lauric acid to dodecane increased greatly when hydrogen was supplied during reaction, suggesting that hydrodeoxygenation of the fatty acids took place.

To learn more about the deoxygenation process of the studied fatty acids over Pt/ZIF-67 membrane/zeolite 5A bead as catalyst, we collected FTIR spectra of the reaction products for the deoxygenation of lauric acid (H_2 and CO_2 atmospheres) as a function of temperature (Figure 7). In the presence of hydrogen (Figure 7a) a clear FTIR peak $\sim 1750\text{ cm}^{-1}$ is present at temperatures between 150 and 280 °C. This peak can be assigned to the stretching bonds in esters group.³⁹ At 300 °C this peak disappears, suggesting that at low reaction temperatures the main products were esters. When the temperature increased, the esters (intermediates) converted to the observed hydrocarbons. Interestingly, under CO_2 atmosphere the peak associated with the esters did not disappear even at 320 °C. This observation suggests that the presence (or absence) of the ester intermediates may influence the final reaction pathway (decarboxylation vs hydrodeoxygenation).

Scheme 1 shows the suggested pathway for the deoxygenation of palmitic and lauric acids over Pt/ZIF-67 membrane/zeolite 5A catalysts. In the presence of He and CO_2 , the fatty acids converted to relative stable ester intermediates (Figure 7b). As the reaction proceeded, these esters transformed directly via decarboxylation into hydrocarbons with one carbon number less. On the other hand, in the presence of H_2 , intermediate esters were also observed. However, these esters disappeared (Figure 7a) in the 280–300 °C temperature range. We hypothesize that these esters rapidly transformed into alcohols.

It is well-known and documented that esters can be readily transformed into alcohols in the presence of reducing (hydrogenating) agents.^{40–44} Specifically, in the presence of hydrogen, aromatic and aliphatic esters can be converted into the corresponding alcohols. In our proposed pathway, the alcohol is hydrogenated resulting in a hydrocarbon with same carbon number (hydrodeoxygenation pathway). Shimizu and co-workers reported a similar ester to alcohol transformation.⁴¹ In their study, they found that the ester formed from lauric acid

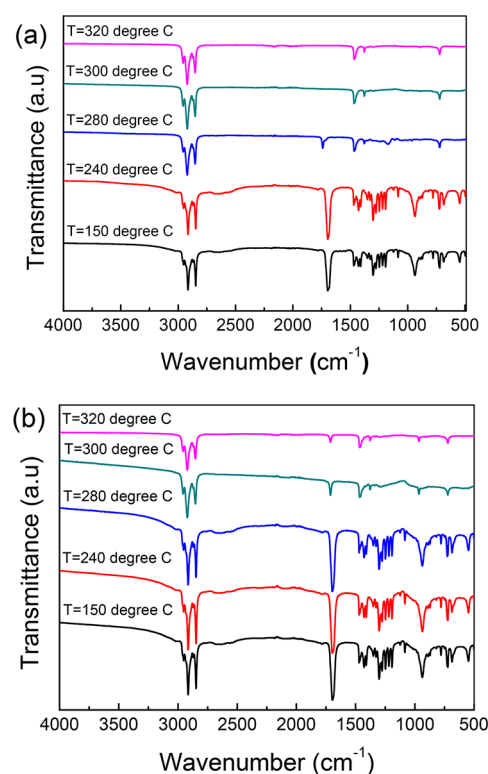
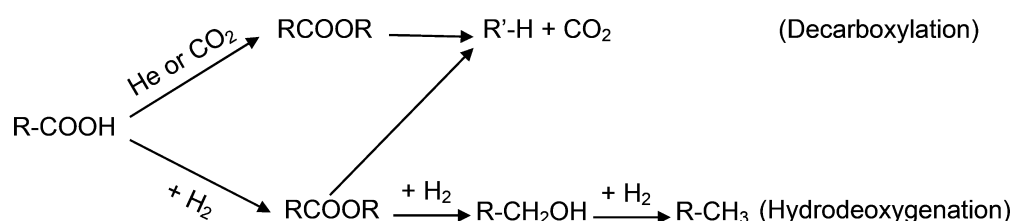


Figure 7. FTIR profiles for product samples obtained from deoxygenation of lauric acid at different reaction temperature under (a) H_2 atmosphere and (b) CO_2 atmosphere. Reaction conditions were the following: catalyst to lauric acid mass ratio = 1:1, pressure = 20 bar, time = 0 h.

underwent hydrogenolysis to form alcohol, which was then hydrogenated to the corresponding alkane.

Table 3 compares the catalytic performance of the state-of-the-art catalysts that have been reported for the deoxygenation of palmitic acid and lauric acid to pentadecane and undecane, respectively. The best catalytic performance for the conversion of palmitic acid to pentadecane corresponds to the Pt supported on carbon and Pd supported on ZrO_2 catalysts (entries 1 and 3). These catalysts displayed pentadecane selectivities as high as 98–100%. However, high noble metal loadings (as high as 5 wt %) were employed for both catalysts. Furthermore, long reaction time (6 h) was required for the Pt supported on carbon catalyst and hydrogen was employed for the Pd supported on ZrO_2 catalyst to achieve such catalytic performance. Although we observed slightly lower pentadecane selectivity ($\sim 92\%$, entry 12), our catalyst composition required very low noble metal loading (0.5 wt %). In addition, the best catalytic performance of our catalysts was observed when CO_2 , a cheap renewable feedstock, was supplied during reaction (no need of hydrogen input). The best catalytic performance for the conversion of lauric acid to undecane corresponds to Pd supported on SiO_2 catalyst employed (entry 15). This catalyst displayed selectivity to undecane as high as $\sim 96\%$. 5 wt % of Pd loading was needed for this catalyst, and the presence of hydrogen was needed to achieve such catalytic performance. On the other hand, our best catalyst (entry 18) displayed selectivity to undecane of $\sim 94\%$. Our catalyst composition required very low noble metal loading (0.5 wt %) and exhibited superior catalytic performance in the presence of CO_2 .

Scheme 1. Suggested Pathway for the Deoxygenation of Fatty Acids over Pt/ZIF-67 Membrane/Zeolite 5A Catalysts under Different Reaction Gas Environments

Table 3. Catalytic Conversion of Palmitic Acid and Lauric Acid over Solid Catalysts^a

entry	catalyst	reaction conditions	mass ratio of metal to palmitic acid	conversion (%)	pentadecane selectivity (%)	ref
1	5 wt % Pt/C	$T = 290\text{ }^{\circ}\text{C}$, $t = 6\text{ h}$	1:200	100	100	45
2	activated carbon	$T = 370\text{ }^{\circ}\text{C}$, $t = 3\text{ h}$		33 ± 13	58 ± 4	23
3	5 wt % Pd/ZrO ₂	$T = 260\text{ }^{\circ}\text{C}$, $P = 12\text{ bar}$, $t = 2\text{ h}$	1:40	98	98	35
4	10% Ni/10% NbO ₂ /SiO ₂	$T = 220\text{ }^{\circ}\text{C}$, $P = 25\text{ bar}$, $t = 24\text{ h}$	1:10	100	13.9	46
5	Ni ₁₀ P/AC	$T = 350\text{ }^{\circ}\text{C}$, $t = 2.5\text{ h}$		99.4	74.9	47
6	Ni(OAc) ₂	$T = 350\text{ }^{\circ}\text{C}$, $t = 4.5\text{ h}$		53.1	35.4	48
7	20 wt % Mo/HZ-C	$T = 260\text{ }^{\circ}\text{C}$, $P = 40\text{ bar}$, $t = 4\text{ h}$	1:25	100	35.1	49
8	4 wt % Ni/HZ-3	$T = 220\text{ }^{\circ}\text{C}$, $P = 40\text{ bar}$	1:125	100	44.0	50
9	NiMCF(9.2T-3D)(R)	$T = 300\text{ }^{\circ}\text{C}$, $t = 6\text{ h}$		86.4	31.8	51
10	5 wt % Pd/CNTs	$T = 260\text{ }^{\circ}\text{C}$, $P = 40\text{ bar}$, $t = 4\text{ h}$	1:40	93.3	85.4	52
11	10 wt % Ni/ZrO ₂	$T = 290\text{ }^{\circ}\text{C}$, $P = 55.2\text{ bar}$, $t = 6\text{ h}$	1:10	97.2	35.6	53
12	0.5 wt % Pt/ZIF-67/zeolite 5A	$T = 320\text{ }^{\circ}\text{C}$, $P = 20\text{ bar}$, $t = 2\text{ h}$	1:200	95	91.7	this study

entry	catalyst	reaction conditions	mass ratio of metal to lauric acid	conversion (%)	undecane selectivity (%)	ref
13	5 wt % Pd/C	$T = 300\text{ }^{\circ}\text{C}$, $P = 13\text{ bar}$		80	98	54
14	Ni(OAc) ₂	$T = 350\text{ }^{\circ}\text{C}$, $t = 4.5\text{ h}$		15.3	24.2	48
15	5 wt % Pd/SiO ₂	$T = 300\text{ }^{\circ}\text{C}$, $P = 15\text{ bar}$, $t = 4\text{ h}$	1:67	100	96	55
16	15 wt % Ni ₂ P/SiO ₂	$T = 300\text{ }^{\circ}\text{C}$, $P = 20\text{ bar}$, WHSV = 6 h^{-1}		98.8	87.9	56
17	5 wt % Pd/C	$T = 300\text{ }^{\circ}\text{C}$, $P = 20\text{ bar}$, $t = 5\text{ h}$	1:200	65	86.2	34
18	0.5 wt % Pt/ZIF-67/zeolite 5A	$T = 320\text{ }^{\circ}\text{C}$, $P = 20\text{ bar}$, $t = 2\text{ h}$	1:200	95	93.5	this study

^aThe best catalytic performance is shown. In entries 3, 4, 5, 7, 8, 10, 11, 15, 16, and 17 hydrogen is used.

4. CONCLUSIONS

The deoxygenation reaction of two saturated fatty acids, palmitic acid and lauric acid, over 0.5 wt % Pt/ZIF-67 membrane/zeolite 5A bead catalysts under different reaction gas atmospheres is demonstrated. Almost complete conversion (% deoxygenation of $\geq 95\%$) of fatty acids was observed over both fresh and recycled catalyst after a 2 h reaction time. These catalysts displayed high selectivity to pentadecane for palmitic acid deoxygenation and high selectivity to undecane for lauric acid deoxygenation. Lower reaction temperature was favorable to obtain high selectivity of long chain hydrocarbons. Shorter chain hydrocarbons (C₇–C₁₄) produced by the cracking of long chain hydrocarbons were observed as secondary products. The recycled catalysts displayed similar catalytic performance as fresh catalysts. Depending on the reaction gas atmosphere, two distinctive reaction pathways were observed: decarboxylation and hydrodeoxygenation. Specifically, it was found that decarboxylation reaction pathway was more favorable in the presence of helium and CO₂, while hydrodeoxygenation pathway strongly competed against the decarboxylation pathway when hydrogen was employed during the deoxygenation reactions. Ester groups were identified as the key reaction intermediates leading to decarboxylation and hydrodeoxygenation pathways.

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Notes

The authors declare no competing financial interest.

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