

Decarboxylation of Oleic Acid to Heptadecane over Pt Supported on Zeolite 5A Beads

Liqu Yang,[†] Kirby L. Tate,[†] Jacek B. Jasinski,[‡] and Moises A. Carreon^{*,†}

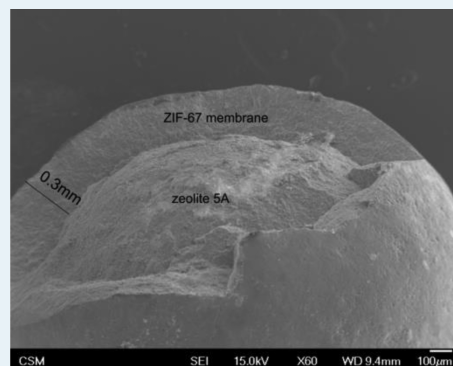
[†]Chemical and Biological Engineering Department, Colorado School of Mines, Golden, Colorado 80401, United States

[‡]Conn Center for Renewable Energy Research, University of Louisville, Louisville, Kentucky 40292, United States

Supporting Information

ABSTRACT: The synthesis of Pt supported on zeolite 5A beads for the decarboxylation of oleic acid to heptadecane is demonstrated. The use of a microporous ZIF-67 crystalline layer on zeolite 5A beads not only improved the heptadecane selectivity but also, most importantly, improved the stability of the resultant catalyst. Heptadecane yields as high as ~81% were observed for the fresh catalysts. The catalysts displayed only low to moderate loss of catalytic activity after two rounds of recycle. To our best knowledge, the catalytic performance of these catalysts is superior to those of the state-of-the-art catalysts at mild reaction conditions. In addition, as compared to powders, beads are much easier to recycle, can be fully recovered, and are more amenable for potential scale-up. The resultant catalysts are promising for the catalytic conversion of fatty acid molecules into gasoline/diesel-range hydrocarbons.

KEYWORDS: decarboxylation, oleic acid, fuel hydrocarbons, Pt, zeolite beads, ZIF-67



Carboxylic acids obtained from biomass raw materials are appealing starting materials in the conversion to linear, paraffinic hydrocarbons. The resultant hydrocarbon products can potentially be used as platform chemicals for the production of fuels, lubricants, and other valuable petrochemicals.¹ Decarboxylation is an effective route for the conversion of carboxylic acids to linear, paraffinic hydrocarbons.^{2–5} The decarboxylation reaction produces hydrocarbons with a linear structure in which the alkyl group of the carboxylic acid is preserved, and the carboxylate group (i.e., one carbon atom and two oxygen atoms) is removed as carbon dioxide. The resultant alkane product has one carbon atom less than the carboxylic acid starting material. Although the decarboxylation reaction does not require a supply of hydrogen as a necessary reactant, it has been demonstrated that the presence of hydrogen is highly desirable to maintain stable catalytic activity.⁶

The decarboxylation of oleic acid over different catalysts is well documented.^{3,7–35} These catalysts include Pt–Re/C,¹¹ Pt/C,^{11–14,35} Pd/C,^{3,12,15–18} activated carbon,^{1,19} molybdenum nitrate, tungsten nitride, platinum nitride, palladium nitride and vanadium nitride supported on γ -Al₂O₃,^{20–23} Pt/SiO₂,¹² hydrotalcite,⁴ Sn-containing layered double hydroxide,²⁴ supported iron nanoparticle,²⁵ Ni/MgO–Al₂O₃,²⁶ H₃PO₄/Al₂O₃,²⁷ Pt/CeO₂,²⁸ natural aluminosilicate as well as nano-sized titanium, magnesium, zirconium, and cerium oxide.^{29,30}

In most of these reports, the support is a catalytically inert material like carbon or a relatively, nonacidic phase material like silica or nonacidic alumina. Recently, our group has reported the catalytic decarboxylation of oleic acid to hydrocarbons over acidic and basic supports including Pt–SAPO-11 and Pt/

chloride Al₂O₃,²¹ Pt/SAPO-34, Pt/DNL-6, Pt/RHO and Pt/hydrotalcite,³² and metal–organic frameworks.³⁴ In general, we have observed an improvement in yields to heptadecane when acidic supports are used. However, the observed yields to heptadecane are still moderate.

Herein, we present the synthesis of “Pt supported on acidic zeolite beads” for the decarboxylation of oleic acid to heptadecane. As compared to powders, beads are much easier to recycle and can be fully recovered. Furthermore, beads are more amenable for potential scale-up. Interestingly, we have found that less Pt (only 1 wt %) is required to achieve high heptadecane selectivities when beads are used as compared to powders. For powders, at least 5 wt % Pt is required to observe only moderate heptadecane selectivities over zeolites SAPO-11,²¹ SAPO-34,³² DNL-6,³² RHO,³² and Cu-, Al-, and Ga-based metal–organic frameworks.³⁴

Zeolite 5A beads used as catalytic supports in this study are shown in Figure S1. Zeolite 5A (with typical chemical composition of Na_xCa_y[(AlO₂)₁₂(SiO₂)₁₂·xH₂O]) beads were chosen because their high chemical and thermal stability. In addition, this aluminosilicate medium pore size zeolite with acidic sites³⁶ is commercially available and is cheaper than other medium pore zeolite beads such as 13X and beta. Previously, we have demonstrated that the acidic supports play an important role in the decarboxylation reaction to obtain improved heptadecane selectivities.^{21,32} This zeolite displays

Received: June 22, 2015

Revised: September 25, 2015

LTA topology and has uniform pores of ~ 0.5 nm. The measured N_2 BET surface area of the 2.5 mm beads was 549 m^2/g . As compared to powders, beads are much easier to recycle and can be fully recovered, and therefore, they are more amenable for potential scale-up for diverse catalytic applications. Figure S1 shows 1 wt % Pt deposited on the zeolite 5A beads (see Supporting Information for experimental details).

The catalytic performance of the 1 wt % Pt/zeolite 5A bead catalyst was evaluated for the decarboxylation of oleic acid at 320 $^\circ C$ and 20 bar. These reaction parameters were chosen on the basis of optimum conditions of our previous studies.^{21,32,34} High degree of decarboxylation was observed for this sample. More specifically, decarboxylation % as high as $\sim 98.7\%$ was observed (see Supporting Information for the experimental method employed to quantify the decarboxylation %). Recently, we have demonstrated that acidic zeolite supports can help in promoting the decarboxylation of fatty acid molecules such as oleic acid.^{21,32} The presence of H_2 promoted the hydrogenation of unsaturated oleic acid to saturated stearic acid which then underwent facile decarboxylation. Catalyst recyclability experiments showed that 1 wt % Pt/zeolite 5A catalysts can be recycled and still maintained high decarboxylation catalytic effectiveness after at least two recycle rounds (Table S1).

Heptadecane selectivity of $\sim 74\%$ was observed for the fresh 1 wt % Pt/zeolite 5A catalyst, corresponding to a heptadecane yield of $\sim 73\%$. In principle, the fact that only 1 wt % Pt is required for observing such high heptadecane selectivity, suggests that Pt is well dispersed on the surface of the beads. This may suggest relatively large values of Thiele modulus (ratio of surface reaction rate to diffusion rate through the pellet³⁷), indicating that the surface reaction is rapid and that the reactant may be consumed very close to the external pellet surface and very little penetrates into the interior of the pellet. Heptadecane selectivity decreased to 52% for the first recycled catalyst and 46% for the second recycled catalyst. This decrease in heptadecane selectivity may be in part explained to the considerable decrease in surface area of the fresh catalyst to the second recycled catalyst (from 530 m^2/g to 230 m^2/g respectively). The lower surface area of the spent catalysts has been commonly observed in porous catalysts for this reaction, and the reduced surface area can be attributed to the incomplete removal of surface carbonaceous species formed during the reaction. Pore volume decreased from fresh to recycled catalysts (Table S2), suggesting that micropores were partially blocked. Raman spectroscopy indicated the presence of surface carbonaceous species in the external surface for a second recycled 1 wt % Pt/zeolite 5A catalyst (Figure S2). Previously, our group found that microporous crystalline phases with pore sizes between ~ 0.35 – 0.38 nm can be beneficial for improving heptadecane selectivity.³² We postulated that potentially a “molecular sieving effect” was in part responsible for this enhanced catalytic behavior.³² On the basis of this premise, and on the fact that transition metals such as Co have demonstrated to be an alternative and viable replacement of Pt to improve catalyst stability,³⁸ we incorporated a cobalt-based metal organic framework membrane (known as ZIF-67) on the surface of the zeolite 5A beads. ZIF-67 is a cobalt-based zeolitic imidazolate framework displaying SOD topology and large pores with diameters of 1.16 nm that are accessible through small pore windows with diameters of 0.34 nm, which has recently received considerable attention due to its desirable properties as catalyst, adsorbent, sensor, and membrane.³⁹

Then, zeolite 5A beads covered with ZIF-67 membrane were impregnated with 1 wt % Pt and evaluated in the decarboxylation of oleic acid to heptadecane.

Figure 1 shows a representative SEM image of a 1 wt % Pt/ZIF-67 membrane/zeolite 5A bead catalyst. SEM shows a

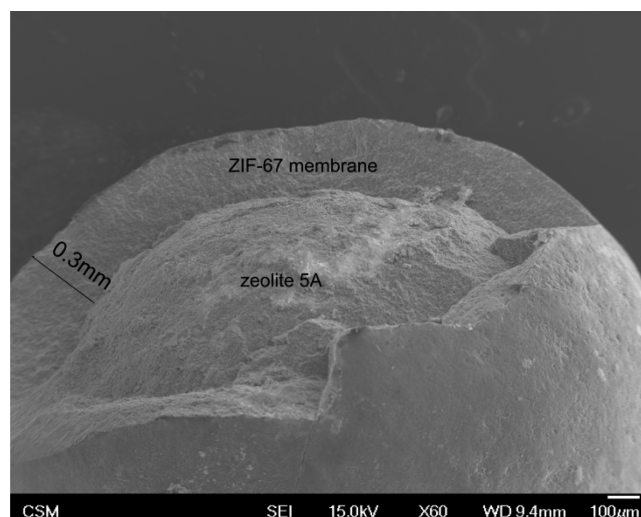


Figure 1. Representative SEM image of a 1 wt % Pt/ZIF-67 membrane/zeolite 5A bead catalyst.

continuous ZIF-67 membrane of ~ 300 μm thickness. Decarboxylation % as high as $\sim 99\%$ was observed for this catalyst (similar to the catalyst without ZIF-67 membrane) with heptadecane selectivity of $\sim 82\%$ for the fresh catalyst (yield $\sim 81\%$). The use of a microporous ZIF-67 crystalline layer improved the heptadecane selectivity, but most importantly improved the stability of the resultant catalyst. The recycled 1 wt % Pt/ZIF-67 membrane/zeolite 5A bead catalysts decreased its performance to 64% and $\sim 60\%$ for the first recycled and second recycled catalysts, respectively. The surface area of the second recycled catalyst decreased only to 402 m^2/g as compared to the 560 m^2/g of the fresh catalyst, indicating a much lower decrease in surface area as compared to the catalyst prepared in the absence of ZIF-67 membrane. Figure 2 shows the XRD patterns of all studied catalysts. All XRDs shows the typical known structure of zeolite 5A which crystallizes in the

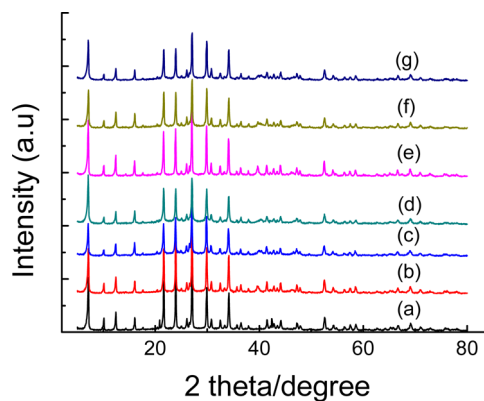


Figure 2. XRD patterns of (a) zeolite 5A beads, (b) fresh Pt/zeolite 5A, (c) first recycled Pt/zeolite 5A, (d) second recycled Pt/zeolite 5A, (e) fresh Pt/ZIF-67/zeolite 5A, (f) first recycled Pt/ZIF-67/zeolite 5A, (g) second recycled Pt/ZIF-67/zeolite 5A.

LTA topology.⁴⁰ Figure 2b–g specifically confirms that the crystalline structure of zeolite 5A is preserved after Pt deposition, after the incorporation of ZIF-67 membrane and after two rounds of recycle, suggesting high structural stability of all catalysts. The N₂ BET surface areas of the fresh and recycled catalysts are shown in Table S3.

The observed heptadecane yields for all the studied catalysts are summarized in Figure 3. Due to the relative high reaction

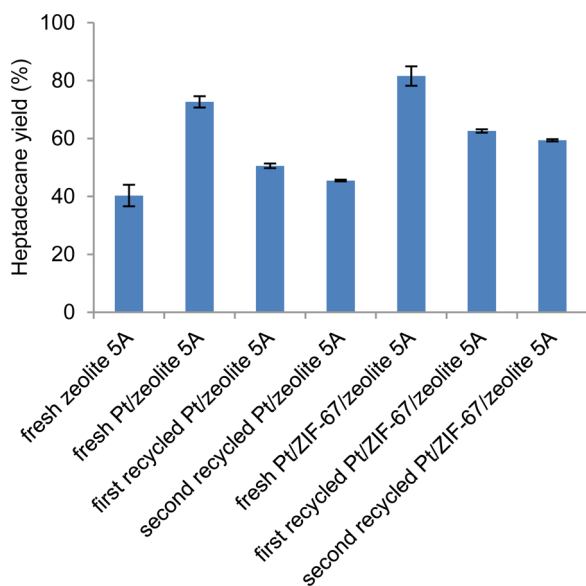


Figure 3. Heptadecane yields of the studied catalysts. Reaction conditions: $P = 20$ bar, $T = 320$ °C, $t = 2$ h, mass ratio of catalyst to oleic acid = 1:1. Error bars reflect the average of two independent catalytic tests.

temperature, some degree of the decarboxylation was observed (thermal non catalytic decarboxylation) in the absence of the catalyst (~14%). It is important to mention that pure zeolite 5A beads displayed yields to heptadecane of only ~38% for the fresh sample and ~24% for the first recycled sample. The detailed liquid product distribution of all studied catalysts (fresh and recycled) is given in Table 1. The components in the liquid product included branched paraffins formed by isomerization of the initially formed heptadecane and lower molecular weight hydrocarbons (mostly C7–C18 paraffins) formed by cracking of the heptadecane. No detectable oleic acid was observed in the products under the prevailing reaction conditions, suggesting total conversion of oleic acid (and supported by

the high observed decarboxylation %). The observed side products were the following: octadecane, heptadecane, dodecane, undecane, decane, nonane, octane, heptane.

In order to have a better understanding of the role of ZIF-67 on the surface of the zeolite 5A beads, we performed TEM and EDX analysis. Figure 4a,b show representative STEM images of

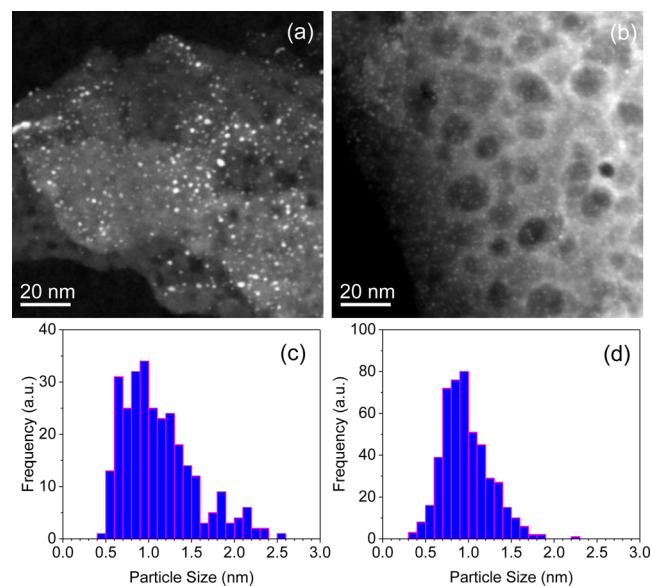


Figure 4. Representative STEMs of fresh (a) 1 wt % Pt/zeolite 5A, (b) 1 wt % Pt/ZIF-67 membrane/zeolite 5A bead catalysts, and Pt particle size distribution of (c) 1 wt % Pt/zeolite 5A and (d) 1 wt % Pt/ZIF-67 membrane/zeolite 5A bead catalysts.

the fresh 1 wt % Pt catalysts without and with ZIF-67 membrane. In both cases, high density of well-dispersed platinum nanoparticles are observed. However, for the sample in which no ZIF-67 was incorporated, some clustering is observed, indicating that Pt nanoparticles dispersed better when ZIF-67 layer is present. Figure 4b shows the presence of some voids ~5–15 nm associated with mesoporosity. The Pt particle histograms shown in Figures 4c,d confirm that for the sample having the ZIF-67 layer, a relatively narrow particle size distribution centered at ~1 nm is observed (Figure 4d). However, for the sample in which no ZIF-67 layer is present (Figure 4c), the size distribution is relatively broad, ranging from ~0.5 nm to ~2.5 nm. STEM shown in Figure 4 suggests a much better dispersion of Pt for the sample prepared in the presence of ZIF-67. The ordered porous structure of ZIF-67

Table 1. Liquid Product Distribution for the Studied Catalysts^a

catalyst	hydrocarbon products								
	octadecane	heptadecane	dodecane	undecane	decane	nonane	octane	heptane	unknown
zeolite 5A	11.36	59.32	3.37	5.65	5.65	5.17	6.72	-	2.77
fresh Pt/zeolite 5A	22.12	74.99	0.39	0.46	0.51	0.52	0.40	0.27	0.33
first recycled Pt/zeolite 5A	46.98	51.67	0.16	0.19	0.23	0.26	0.21	0.17	0.13
second recycled Pt/zeolite 5A	52.05	46.00	0.30	0.34	0.34	0.28	0.18	0.05	0.46
fresh Pt/ZIF-67/zeolite 5A	17.03	79.89	0.32	0.37	0.45	0.50	0.45	0.36	0.62
first recycled Pt/ZIF-67/zeolite 5A	34.72	63.64	0.20	0.28	0.29	0.33	0.25	0.18	0.11
second recycled Pt/ZIF-67/zeolite 5A	38.91	60.12	0.08	0.10	0.15	0.19	0.17	0.17	0.11
fresh Pt/ZIF-8/zeolite 5A	40.92	57.03	0.26	0.34	0.41	0.42	0.31	0.15	0.15
first recycled Pt/ZIF-8/zeolite 5A	66.85	32.85	0.08	0.07	0.04	-	-	-	0.09

^aReaction conditions: $P = 20$ bar, $T = 320$ °C, $t = 2$ h, mass ratio of catalyst to oleic acid = 1:1.

Table 2. Comparison of the Catalytic Conversion of Oleic Acid to Heptadecane through Different Catalysts^a

entry	catalyst	reaction conditions	metal/oleic acid (wt %)	conversion (%)	heptadecane selectivity (%)	ref
1	5 wt % Pd/C	$P = 15 \text{ bar}$, $T = 300 \text{ }^\circ\text{C}$, $t = 3 \text{ h}$	1:92	11	12	16
2	5 wt % Pd/C	$P = 27 \text{ bar}$, $T = 360 \text{ }^\circ\text{C}$, $t = 6 \text{ h}$	1:115	99	26	3
3	activated carbon	$T = 370 \text{ }^\circ\text{C}$, $t = 3 \text{ h}$	-	80 ± 4	7 ± 1	1
4	SnAlMg-2	$T = 300 \text{ }^\circ\text{C}$, $t = 6 \text{ h}$	1:75	71.1	3.7	24
5	5 wt % Pt/C	$T = 623 \text{ K}$, $t = 3 \text{ h}$	1:409	99	71	12
6	$\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$	$T = 300 \text{ }^\circ\text{C}$, $t = 6 \text{ h}$	1:40	94.6	11	30
7	5 wt % Pt-chlorided alumina	$P = 20 \text{ bar}$, $T = 325 \text{ }^\circ\text{C}$, $t = 2 \text{ h}$	1:360	98	64	21
8	Fe-MSN	$P = 30 \text{ bar}$, $T = 290 \text{ }^\circ\text{C}$, $t = 6 \text{ h}$	1:4.7	100	12	25
9	Pt-Re/C	$P = 0.35 \text{ MPa}$, $T = 300 \text{ }^\circ\text{C}$, $t = 9 \text{ h}$	1:769	92	40	11
10	Pd/Si-C-4	$P = 1.5 \text{ MPa}$, $T = 300 \text{ }^\circ\text{C}$, $t = 1 \text{ h}$	1:89	90	31	13
11	$\text{Co}_{0.5}\text{Mo}_{0.5}$	$T = 300 \text{ }^\circ\text{C}$, $t = 3 \text{ h}$	1:40	88.1	6.1	31
12	Pt/SAPO-34	$P = 20 \text{ bar}$, $T = 325 \text{ }^\circ\text{C}$, $t = 2 \text{ h}$	1:400	98	66.9	32
13	$\text{MgO-Al}_2\text{O}_3$	$T = 673 \text{ K}$, $t = 3 \text{ h}$	1:20	98	6.93	4
14	1 wt % Pd/C	$T = 300 \text{ }^\circ\text{C}$, $t = 5.5 \text{ h}$	-	12	39	17
15	5 wt % Pt/ $\gamma\text{-Al}_2\text{O}_3$	$P = 20 \text{ bar}$, $T = 325 \text{ }^\circ\text{C}$, $t = 5 \text{ h}$	-	100	-	22
16	NiWC/Al-SBA-15	4 h in supercritical water	1:44	30.7	0.72	33
17	activated carbon	$P = 24.1 \text{ MPa}$, $T = 370 \pm 2 \text{ }^\circ\text{C}$	-	99.4 ± 0.5	80.6 ± 4	19
18	Pd/carbon bead	$P = 20 \text{ atm}$, $T = 573 \text{ K}$, $t = 9 \text{ h}$	1:66	100	70.5	18
19	$\text{Pt}_3\text{Sn/C}$	$T = 350 \text{ }^\circ\text{C}$, $t = 2 \text{ h}$	1:113	100	60	14
20	5 wt % Pd/ $\gamma\text{-Al}_2\text{O}_3$	$P = 5 \text{ MPa}$, $T = 330 \text{ }^\circ\text{C}$, LHSV = 2 h^{-1}	-	94.6	72	23
21	5 wt % Pt/Ga-MOF	$P = 20 \text{ bar}$, $T = 320 \text{ }^\circ\text{C}$, $t = 2 \text{ h}$	1:360	91	21.5	34
22	5% Pt/C	$T = 330 \text{ }^\circ\text{C}$, $t = 2 \text{ h}$	1:199	-	18	35
23	fresh Pt/zeolite 5A	$P = 20 \text{ bar}$, $T = 320 \text{ }^\circ\text{C}$, $t = 2 \text{ h}$	1:100	98.74	72.6 ± 2	this study
24	fresh Pt/ZIF-67/zeolite 5A	$P = 20 \text{ bar}$, $T = 320 \text{ }^\circ\text{C}$, $t = 2 \text{ h}$	1:100	98.70	81.5 ± 3	this study

^aOnly the best catalytic performance of each reference is shown in the table. Note: In Entries 2, 6, 7, 8, 12, 14, 15, 18, 20, 21, 23, and 24, hydrogen is used. In Entries 4, 6, 11, and 13, the ratio corresponds to catalyst/oleic acid (wt %).

serves as a more uniform region in which Pt particles can be distributed. In addition, TEM histograms indicate that smaller particles with narrow size distribution prevail for the catalysts having the ZIF-67 membrane. EDX analysis provided useful information on the degree of Pt leaching for the recycled catalysts. A lower Pt% loss was observed when ZIF-67 was used as membrane in the catalysts ($\sim 15\%$ Pt loss when ZIF-67 was used versus $\sim 26\%$ loss in the absence of ZIF-67 after second recycle). This behavior may be related to a better “grafting” of Pt particles within the ZIF-67 porous structure. Our results suggest that the addition of ZIF-67 layer, in general: (1) promoted better Pt particle dispersion on the beads as confirmed by STEM; (2) reduced Pt leaching after reaction, resulting in improved recyclable catalysts as confirmed by EDX; and (3) the presence of Co as coordinating metal, resulted in a more active (to heptadecane and octadecane) and stable catalysts (lower catalytic activity reduction after reaction was observed). A recent study has demonstrated that cobalt coordinated with platinum shows high catalytic activity and stability for the hydrogenation of oxygen (oxygen reduction reaction).⁴¹ The authors attributed the enhanced activity and stability of the catalyst to the presence of a stable Pt-Co intermetallic. However, in our case, there is no experimental evidence that the formation of Pt-Co intermetallic can take place. Therefore, it is likely that coordinated cobalt in the ZIF-67 is responsible for the promoter role. In addition, due to the reducing conditions prevailing during reaction, we cannot exclude the presence of metallic Co.

Even in the absence of ZIF-67 (no cobalt present), the catalysts were active. Therefore, the main role of cobalt is to act as cocatalyst or promoter. There are numerous examples in the literature in which Co has been used as cocatalyst (promoter)

for hydrodeoxygenation and decarboxylation reactions. For example: Centeno et al.⁴² reported the use of Co-noble-metal based catalysts for the hydrodeoxygenation reaction of different model molecules containing carbonyl, carboxyl, hydroxyl, and methoxy groups. They found that the presence of Co favored the decarboxylation activity. A synergistic effect between the noble metal (Pt, Pd, Rh, Ru) was responsible for this catalytic behavior. Wang et al.⁴³ attributed also a positive synergistic effect when Co was incorporated into Mo-based catalysts for an enhanced catalytic activity for hydrodeoxygenation of bio-oils. Furthermore, cobalt-based catalysts enhance the C(sp²)-O cleavage via direct deoxygenation pathway.⁴⁴ Deoxygenation is the direct pathway for the conversion of oleic acid into one of the main observed products: octadecane. Interestingly, we observed that the Co/Pt ratio correlates directly to the octadecane yield (Table S4).

To prove the benefits of having Co in the porous structure, we prepared an isostructural layer of ZIF-8 (in which instead of using Co, Zn was employed as coordinating metal). When this layer (known as zeolitic imidazolate framework ZIF-8)³⁸ was employed, the yield to heptadecane for the fresh catalyst was only 57% (Table 1), suggesting that indeed Co helps to promote the formation of higher yields of heptadecane and octadecane, as well as to improve catalyst stability. Pt leaching was more pronounced when ZIF-8 layer was employed vs ZIF-67 layer. More specifically, when ZIF-67 was employed, only $\sim 15\%$ of Pt leaching for the second recycled catalyst was observed. On the other hand, when ZIF-8 was employed, Pt leaching increased to 24% for the second recycled catalyst. This observation together with the poor Pt dispersion (Pt particle size distribution in the $\sim 1\text{--}20 \text{ nm}$ range) on ZIF-8 shown in

Figure S3 may explain the lower heptadecane yields observed for the ZIF-8 composed samples.

In our studies, zeolite 5A beads acted as acid^{36,45} catalytic support, providing a large surface area, and playing an important role on the dispersion of Pt. Our group^{32,34} and independent groups^{46,47} have observed that acidic supports promote a better (higher) dispersion of the noble metal and therefore result in improved catalytic activity for decarboxylation and dehydroxylation reactions. STEM revealed that a better Pt dispersion was achieved when Pt was deposited on zeolite 5A as compared to neutral carbon pellets. In the case of neutral carbon pellets, a broader Pt nanoparticle size distribution and clustering was observed (Figure S4).

It is important to mention that the reduction of Pt content (leaching) and the reduction in surface area of the Pt/zeolite 5A and Pt/ZIF-67/zeolite 5A catalysts after recycling correlated to the decrease in heptadecane yield. More specifically, the higher the reduction on Pt content and surface area, the lower the heptadecane yield.

Another important observation was that the yield of octadecane increased in the following order: second recycled > first recycled > fresh. Interestingly, the C/Pt ratio correlated with the octadecane yield. More specifically, the yield of octadecane increased when the C/Pt ratio increased (Figure S5 and Table S5). It has been demonstrated that carbonaceous species can have a positive effect for hydrotreating processes⁴⁸ including oxygen removal (which is the case in the conversion of oleic acid to octadecane). It has been hypothesized that a geometrical effect by which carbonaceous species may isolate the catalytic active species and stabilize them against sintering.⁴⁷ Another possibility is that these carbonaceous species may reduce the interaction of the catalytic active phase and the support, resulting in an enhanced activity.⁴⁹

Table 2 compares the state-of-the-art catalysts which have been employed specifically for the catalytic conversion of oleic acid to heptadecane. Among all these catalysts, 1 wt % Pt/ZIF-67/zeolite 5A catalyst and the recently reported activated carbon¹⁹ show the highest yields to heptadecane. Although both types of catalysts show very similar heptadecane yields (~80%), the Pt/ZIF-67/zeolite 5A catalyst of this study effectively catalyzes the decarboxylation reaction at mild pressure and temperature (20 bar, 320 °C), as compared to 240 bar and at least 370 °C required for the activated carbon.

In conclusion, we have demonstrated the synthesis of Pt-supported zeolite 5A beads for the decarboxylation of oleic acid to heptadecane. The use of a microporous ZIF-67 crystalline layer on 5A zeolite beads improved the heptadecane selectivity, but most importantly, it improved the stability of the resultant catalyst. Heptadecane yields as high as ~81% were observed for the fresh catalysts. The catalysts displayed only a low loss of catalytic activity after two rounds of recycle. To our best knowledge, the catalytic performance of 1 wt % Pt/ZIF-67/zeolite 5A bead catalysts is superior to those of the state-of-the-art catalysts at mild reaction conditions. As compared to powders, beads are much easier to recycle and can be fully recovered. For instance, from our previous studies on powder-catalysts,^{21,32,34} only ~80% of the catalyst mass can be recovered after recycling, whereas for beads, 100% of the catalyst is recovered. Furthermore, beads are more amenable for potential scale-up. Currently, we are exploring the effect of reaction time, temperature, pressure, and Pt content to better understand kinetics of this reaction.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b01913.

Detailed catalyst synthesis, catalyst characterization, reaction procedures, and product analysis methods; digital pictures of representative catalysts, decarboxylation % results, N₂ BET surface areas, product distribution of Pt-ZIF-8 membrane-zeolite 5A catalyst (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: mcarreon@mines.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

M.A.C. thanks the Coors foundation for financial support of this work. J.B.J. acknowledges support from National Science Foundation EPSCoR program (award no. 1355438). We thank Xuhui Feng for helping with XRD.

■ REFERENCES

- (1) Fu, J.; Shi, F.; Thompson, L. T., Jr.; Lu, X. Y.; Savage, P. E. *ACS Catal.* **2011**, *1*, 227–231.
- (2) Snåre, M.; Kubičková, I.; Mäki-Arvela, P.; Eränen, K.; Murzin, D. Y. *Ind. Eng. Chem. Res.* **2006**, *45*, 5708–5715.
- (3) Snåre, M.; Kubičková, I.; Mäki-Arvela, P.; Chichova, D.; Eränen, K.; Murzin, D. Y. *Fuel* **2008**, *87*, 933–945.
- (4) Na, J. G.; Yi, B. E.; Kim, J. N.; Yi, K. B.; Park, S. Y.; Park, J. H.; Kim, J. N.; Ko, C. H. *Catal. Today* **2010**, *156*, 44–48.
- (5) Mäki-Arvela, P.; Rozmysłowicz, B.; Lestari, S.; Simakova, O.; Eränen, K.; Salmi, T.; Murzin, D. Y. *Energy Fuels* **2011**, *25*, 2815–2825.
- (6) Maier, W. F.; Roth, W.; Thies, I.; Ragué Schleyer, P. V. *Chem. Ber.* **1982**, *115*, 808–812.
- (7) Twaig, F. A.; Zabidi, N. A. M.; Bhatia, S. *Ind. Eng. Chem. Res.* **1999**, *38*, 3230–3237.
- (8) Craig, W. K.; Soveran, D. W. U.S. Patent 4,992,605, February 12, 1991.
- (9) Lima, D. G.; Soares, V. C. D.; Ribeiro, E. B.; Carvalho, D. A.; Cardoso, E. C. V.; Rassi, F. C.; Mundim, K. C.; Rubim, J. C.; Suarez, P. A. Z. *J. Anal. Appl. Pyrolysis* **2004**, *71*, 987–996.
- (10) Arend, M.; Nonnen, T.; Hoelderich, W. F.; Fischer, J.; Groos. *Appl. Catal., A* **2011**, *399*, 198–204.
- (11) Vardon, D. R.; Sharma, B. K.; Jaramillo, H.; Kim, D.; Choe, J. K.; Ciesielski, P. N.; Strathmann, T. J. *Green Chem.* **2014**, *16*, 1507–1520.
- (12) Na, J. G.; Yi, B. E.; Han, J. K.; Oh, Y. K.; Park, J. H.; Jung, T. S.; Han, S. S.; Yoon, H. C.; Kim, J. N.; Lee, H.; Ko, C. H. *Energy* **2012**, *47*, 25–30.
- (13) Sari, E.; Kim, M.; Salley, S. O.; Simon Ng, K. Y. *Appl. Catal., A* **2013**, *467*, 261–269.
- (14) Yeh, T. M.; Hockstad, R. L.; Linic, S.; Savage, P. E. *Fuel* **2015**, *156*, 219–224.
- (15) Ford, J. P.; Thapaliya, N.; Kelly, M. J.; Roberts, W. L.; Lamb, H. H. *Energy Fuels* **2013**, *27*, 7489–7496.
- (16) Immer, J. G.; Kelly, M. J.; Lamb, H. H. *Appl. Catal., A* **2010**, *375*, 134–139.
- (17) Simakova, I.; Rozmysłowicz, B.; Simakova, O.; Mäki-Arvela, P.; Simakov, A.; Murzin, D. Y. *Top. Catal.* **2011**, *54*, 460–466.
- (18) Dragu, A.; Kinayyigit, S.; García-Suárez, E. J.; Florea, M.; Stepan, E.; Velea, S.; Tanase, L.; Collière, V.; Philippot, K.; Granger, P.; Parvulescu, V. I. *Appl. Catal., A* **2015**, *504*, 81–91.
- (19) Popov, S.; Kumar, S. *Energy Fuels* **2015**, *29*, 3377–3384.

- (20) Monnier, J.; Sulimma, H.; Dalai, A.; Caravaggio, G. *Appl. Catal., A* **2010**, *382*, 176–180.
- (21) Ahmadi, M.; Macias, E. E.; Jasinski, J. B.; Ratnasamy, P.; Carreon, M. A. *J. Mol. Catal. A: Chem.* **2014**, *386*, 14–19.
- (22) Madsen, A. T.; Ahmed, E. H.; Christensen, C. H.; Fehrmann, R.; Riisager, A. *Fuel* **2011**, *90*, 3433–3438.
- (23) Srifa, A.; Faungnawakij, K.; Itthibenchapong, V.; Assabumrungrat, S. *Chem. Eng. J.* **2015**, *278*, 249–258.
- (24) Tong, D. S.; Zhou, C. H.; Li, M. Y.; Yu, W. H.; Beltramini, J.; Lin, C. X.; Xu, Z. P. *Appl. Clay Sci.* **2010**, *48*, 569–574.
- (25) Kandel, K. J.; Anderegg, W.; Nelson, N. C.; Chaudhary, U.; Slowing, I. I. *J. Catal.* **2014**, *314*, 142–148.
- (26) Roh, H. S.; Eum, I. H.; Jeong, D. W.; Yi, B. E.; Na, J. G.; Ko, C. H. *Catal. Today* **2011**, *164*, 457–460.
- (27) Araujo, L. R. R.; Scofield, C. F.; Pastura, N. M. R.; Gonzalez, W. A. *Mater. Res.* **2006**, *9*, 181–184.
- (28) Levasseur, B.; Renard, B.; Barbier, J., Jr.; Duprez, D. *React. Kinet. Catal. Lett.* **2006**, *87*, 269–279.
- (29) Gasanov, A. G.; Azizov, A. G.; Khalilova, S. R.; Ayubov, I. G.; Gurbanova, M. M.; Alieva, S. T. *Russ. J. Appl. Chem.* **2014**, *87*, 214–216.
- (30) Shim, J. O.; Jeong, D. W.; Jang, W. J.; Jeon, K. W.; Jeon, B. H.; Cho, S. Y.; Roh, H. S.; Na, J. G.; Ko, C. H.; Oh, Y. K.; Han, S. S. *Renewable Energy* **2014**, *65*, 36–40.
- (31) Shim, J. O.; Jeong, D. W.; Jang, W. J.; Jeon, K. W.; Kim, S. H.; Jeon, B. H.; Roh, H. S.; Na, J. G.; Oh, Y. K.; Han, S. S.; Ko, C. H. *Catal. Commun.* **2015**, *67*, 16–20.
- (32) Ahmadi, M.; Nambo, A.; Jasinski, J. B.; Ratnasamy, P.; Carreon, M. A. *Catal. Sci. Technol.* **2015**, *5*, 380–388.
- (33) Alwan, B. A.; Salley, S. O.; Simon Ng, K. Y. *Appl. Catal., A* **2015**, *498*, 32–40.
- (34) Yang, L.; Ruess, G. L.; Carreon, M. A. *Catal. Sci. Technol.* **2015**, *5*, 2777–2782.
- (35) Fu, J.; Lu, X. Y.; Savage, P. E. *ChemSusChem* **2011**, *4*, 481–486.
- (36) Batonneau-Gener, I.; Degorce, S.; Ayrault, P.; Ducreux, O.; Magnoux, P.; Mignard, S. *Stud. Surf. Sci. Catal.* **2008**, *174*, 857–860.
- (37) Fogler, H. S.; *Elements of Chemical Reaction Engineering*; Prentice Hall PTR: New York, 2004; p 821.
- (38) Guo, S. J.; Zhang, S.; Wu, L. H.; Sun, S. H. *Angew. Chem., Int. Ed.* **2012**, *51*, 11770–11773.
- (39) Banerjee, R.; Phan, A.; Wang, B.; Knobler, C.; Furukawa, H.; O’Keeffe, M.; Yaghi, O. M. *Science* **2008**, *319*, 939–943.
- (40) Peralta, D.; Chaplais, G.; Simon-Masseron, A.; Barthelet, K.; Pirngruber, G. D. *Ind. Eng. Chem. Res.* **2012**, *51*, 4692–4702.
- (41) Wang, D.; Xin, H. L.; Hovden, R.; Wang, H.; Yu, Y.; Muller, D. A.; DiSalvo, F. J.; Abruna, H. D. *Nat. Mater.* **2013**, *12*, 81–87.
- (42) Centeno, A.; Maggi, R.; Delmon, B. *Stud. Surf. Sci. Catal.* **1999**, *127*, 77–84.
- (43) Wang, W.; Yang, Y.; Luo, H.; Hu, T.; Liu, W. *Catal. Commun.* **2011**, *12*, 436–440.
- (44) Bui, V. N.; Laurenti, D.; Delichere, P.; Geantet, C. *Appl. Catal., B* **2011**, *101*, 246–255.
- (45) Díaz, E.; Ordóñez, S.; Vega, A.; Coca, J. J. *Chromatogr A* **2004**, *1049*, 139–146.
- (46) Wang, Y.; Fang, Y.; He, T.; Hu, H.; Wu, J. *Catal. Commun.* **2011**, *12*, 1201–1205.
- (47) Hong, D. Y.; Miller, S. J.; Agrawal, P. K.; Jones, C. W. *Chem. Commun.* **2010**, *46*, 1038–1040.
- (48) Glasson, C.; Geantet, C.; Lacroix, M.; Labruyere, F.; Dufresne, P. J. *Catal.* **2002**, *212*, 76–85.
- (49) Visers, J. P. R.; Mercx, F. P. M.; Bouwens, S. M. A.; de Beer, V. H. J.; Prins, R. J. *Catal.* **1988**, *114*, 291–302.