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(54) Title: SINGLE-STEP CATALYTIC PROCESSES FOR PRODUCTION OF BRANCHED, CYCLIC, AROMATIC AND
CRACKED HYDROCARBONS FROM FATTY ACIDS

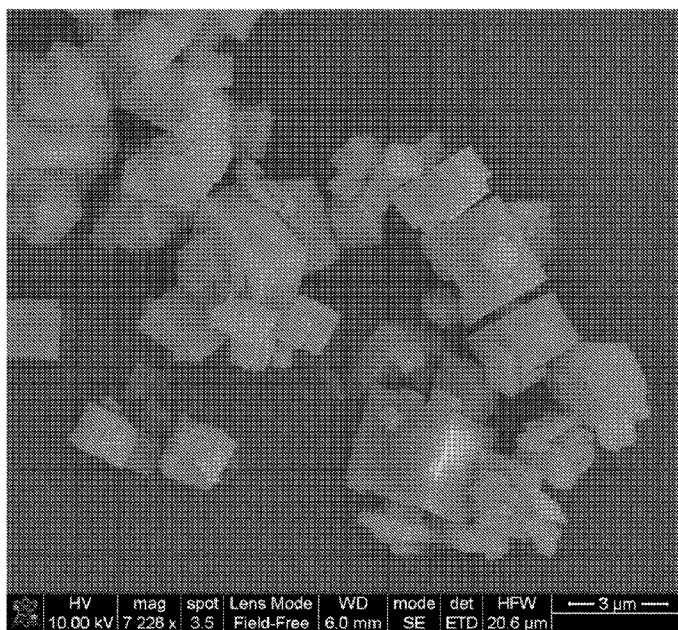


FIG. 1A

(57) Abstract: A catalytic process is provided which produces in a single reaction branched, cyclic and aromatic hydrocarbons, or cracked straight-chain hydrocarbons, from fatty acids in which the fatty acids are reacted over a multifunctional catalyst and undergo both decarboxylation and further conversion (isomerization, cyclization, aromatization, or cracking) to form reaction products useful as fuels and for other applications that require a source of energy, or as feedstock for hydrocarbon-based commercial products such as surfactants, solvents and lubricants.

**Declarations under Rule 4.17:**

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
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UNITED STATES PATENT OFFICE AS RECEIVING OFFICE**UNITED STATES NONPROVISIONAL PATENT APPLICATION****SINGLE-STEP CATALYTIC PROCESSES FOR PRODUCTION OF BRANCHED, CYCLIC, AROMATIC AND CRACKED HYDROCARBONS FROM FATTY ACIDS****Cross Reference to Related U.S. Application**

[0001] This international application claims the benefit of priority to U.S. Provisional Application No. 61/948,139, which was filed on March 5, 2014.

FIELD OF INVENTION

[0002] The embodiments described herein relate to a single step conversion process in which fatty acids (i.e., carboxylic acids) – which can be obtained from biomass and other natural or industrial sources – undergo decarboxylation over a supported catalyst along with further transformation through isomerization, cyclization, aromatization, and cracking, to produce hydrocarbon reaction products which are suitable for use as fuels, surfactants, solvents, lubricants, and other derivatives and commercial products.

BACKGROUND

[0003] Biofuel production technologies have recently received considerable attention for many reasons, including a desire to develop viable alternatives to petroleum-based transportation fuels and the lower CO₂ emission of biofuels compared to such conventional fuels. Without limitation, some of the natural sources of biofuels are natural oils and fats (e.g., animal fats, plant and seed oils). These generally are complex mixtures of triglycerides, which are fatty acid esters of glycerol. The fatty acid esters can be converted to fatty acids through hydrolysis, according to methods known in the art. The carbon chain lengths of fatty acids from natural sources range from about 12-24 carbons, with C₁₂, C₁₆, and C₁₈ fatty acids tending to be the most abundant. While biofuels, which are sometimes referred to as

hydrocarbon fuels, are obtained from crude petroleum oil through a series of conventional steps, it is desirable to produce such fuels and downstream products using such hydrocarbons from alternative, renewable sources, including but not limited to feedstocks of biological origin

[0004] Deoxygenation refers to removing oxygen from fatty acids leading to the formation of paraffinic hydrocarbons. This pathway is one of the general ways used for obtaining paraffinic hydrocarbons (which do not occur naturally in large supply) for use as biofuels and other products. Such paraffinic hydrocarbons can potentially serve as, or be converted to, direct replacements or drop-in fuels for traditional petroleum-derived liquid transportation fuels, as well as paraffinic petrochemical feedstocks.

[0005] Decarboxylation also produces these hydrocarbons from fatty acids, which are readily available in the lipid portion of biomass raw materials, resulting in linear paraffinic hydrocarbons. The isomerization and cyclization of the resulting linear paraffins produces branched and cyclic hydrocarbons, which are more desirable for some uses due to their properties. The fact that biomass raw materials are in relatively large supply increases the desirability of this approach. For example, the lipid portions of plant oils, animal fats, animal oils and algae oils are a ready source of triglyceride esters, which are converted to fatty acids through methods known to persons of ordinary skill in the art, such as hydrolysis, thermal hydrolysis or acid hydrolysis, all methods well known for decades to practitioners in the field

[0006] Several possible reaction pathways are useful for producing straight-chain hydrocarbons from fatty acids through deoxygenation. One is through direct removal of the carboxyl group by releasing carbon dioxide (decarboxylation). Another is by releasing carbon monoxide (decarbonylation). In some cases, decarboxylation of fatty acids is

preceded by hydrogenation of double bonds so that paraffinic hydrocarbons are produced following decarboxylation.

[0007] In previous studies of liquid-phase deoxygenation of free fatty acids, metals such as Ni, Ni/Mo, Ru, Pd, Pd/Pt, Pt, Ir, Os and Rh supported on different supports were evaluated, most commonly under elevated temperatures and pressures. For example, Murzin, et al. reported on the deoxygenation of stearic acid over Pd catalysts supported on carbon, "Heterogeneous catalytic deoxygenation of stearic acid for production of biodiesel." *Ind Eng Chem Res* (2006); 45:5708-15. Through the release of carbon dioxide, the decarboxylation of stearic acid tends to produce heptadecane.

[0008] The nature of the carrier gas also influences the conversion and selectivity values of deoxygenation reactions. For example, Maier et al. reported on the deoxygenation of aliphatic and aromatic fatty acids over Pd/SiO₂ and Ni/Al₂O₃ catalysts at 330°C in different environments (H₂ or N₂), "Gas Phase Decarboxylation of Carboxylic Acids, *Chemische Berichte* (1982); 115:808-812. Their findings included that the presence of hydrogen is desirable for maintaining stable catalytic activity during the decarboxylation reaction. By contrast, no deoxygenation occurred in a nitrogen atmosphere. Snare et al. further conducted liquid phase deoxygenation experiments in a continuous flow reactor under Ar and H₂ atmosphere and solvent-free conditions using a Pd/C catalyst, with the formation of hydrocarbons, mainly olefins and aromatics, below 10 mol%. "Catalytic deoxygenation of unsaturated renewable feedstocks for production of diesel fuel hydrocarbons," *Fuel* (2008); 87: 933-945.

[0009] However, although various catalytic deoxygenation approaches for converting fatty acids such as stearic acid (saturated) and oleic acid (unsaturated) to straight-chain hydrocarbons have been reported, generally in these studies the conversion rate was fairly

low. Such approaches generally use supports formed from catalytically inert material (e.g., carbon) or relatively non-acidic components (e.g., silica or non-acidic alumina). Further, the yields obtained were generally straight-chain normal paraffin hydrocarbon (mainly n-C₁₂ to n-C-20) mixtures. Because of their high cetane number, they generally have excellent performance. However, the pour point of these paraffin mixtures is high so there is a need to transform their structure to make them compatible as diesel blending components (the pour point should be below 5°C).

[00010] Accordingly, for many hydrocarbon products, the branched isomeric forms or their cyclic or aromatic counterparts are desired for properties such as lower pour points. These are obtained through further transformation of the decarboxylated hydrocarbon occurring in the reaction over the same catalyst, including isomerization, cyclisation, aromatization, and hydrocracking. For example, it is known that isomerization of the normal to isoparaffins is used to lower their pour points, but previous attempts to accomplish this have not produced needed results in terms of selectivity for the desired isomers. Previous approaches, however, have employed a two-step process with the first step being deoxygenation, and the second being isomerization, cyclisation, or aromatization using a different catalyst thus carrying with it higher production costs.

[00011] In view of this, it would be advantageous to accomplish the deoxygenation of fatty acids and their further transformation (including but not limited to isomerization/cyclisation/hydrocracking of the intermediate linear paraffins) with a single, multifunctional catalyst in a single reactor for the conversion of lipid biomass material to ‘drop-in’ hydrocarbon transport fuels, like motor and aviation gasoline, among other commercial products manufactured from the products of the subject reactions. For example, the ability to do so reduces the amount of time it takes to obtain the desirable products,

increases efficiency, and increases cost-effectiveness. Further, the same efficiencies would make it advantageous for such a process to also hydrogenate any unsaturated fatty acids contained in the feedstock, thus producing a hydrocarbon that is less prone to instability (e.g., oxidation and heat degradation) due to the presence of double bonds. The present embodiments provide these features and advantages.

SUMMARY OF EMBODIMENTS

[00012] Present embodiments provide, in a single reaction, the catalytic decarboxylation and further transformation of fatty acids, (including but not limited to oleic acid), to paraffins, branched isoparaffins, shorter chain-length hydrocarbons formed through hydrocracking of the intermediates, and cyclic and aromatic hydrocarbons. Both decarboxylation and further transformation occur by contacting the reactants with platinum supported on small pore zeolites (i.e., SAPO-34, DNL-6, and RHO), in addition to platinum supported on hydrotalcite. The subject fatty acids have a general formula $R-COOH$ and contain about 12-24 carbons.

[00013] The supported catalysts disclosed and/or claimed herein include Pt/SAPO-34, Pt/DNL-6, Pt/RHO, and Pt/hydrotalcite. The platinum is incorporated with the support through various methods which are known to persons skilled in the art, including impregnation of the support using platinum salts. Temperature, selection of support, and platinum source are factors which determine the product profile, as further shown herein.

[00014] One such catalyst, Pt/Sapo-34 advantageously provides not only a higher degree of decarboxylation with higher selectivity to heptadecane than the other catalysts, but also favorable selectivity to dodecylbenzene, an aromatic hydrocarbon used as a starting material in the manufacture of detergents and other products.

[00015] Present embodiments disclose catalytic decarboxylation and further conversions of fatty acids to paraffins, branched and aromatic hydrocarbons over Pt supported on small pore zeolites and hydrotalcite. The influence of support, platinum source, and reaction temperature on the decarboxylation of oleic acid are provided for illustrative purposes. During such a decarboxylation process, an increase of reaction temperature increased the degree of decarboxylation and selectivity to heptadecane. Pt-SAPO-34 was one catalyst used. Besides a high degree of decarboxylation, Pt-SAPO-34 displayed a high selectivity to heptadecane and dodecylbenzene among the products. Branched isomers, cracked (mostly < C17) paraffins, alkenes such as undecene and dodecene, and fatty acids such nonanoic acid and decanoic acid were observed as side products. Upon the decarboxylation of oleic acid, the further isomerization of the initially formed linear heptadecane to branched isomers is suppressed in the narrow pores of SAPO-34 due to restricted transition state shape selectivity limitations in the pore system of SAPO-34. Catalyst acidity, dispersion of Pt and pore diameter of the support were factors in determining product selectivity.

[00016] The steps of the process according to multiple embodiments and alternatives comprise contacting the fatty acids with a solid catalyst containing at least one metal over a support, wherein the metal is platinum, and the support is chosen from SAPO-34, SAPO-11, DNL-6, RHO, and hydrotalcite. Generally, the hydrocarbon products formed contain one (or more) fewer carbon atoms than the starting material. Herein, “single-step” refers to a single reaction, having at least one intermediate; “conversion” and “transformation” are synonymous, with either referring to chemical changes of an intermediate by isomerization, cyclization, aromatization, or cracking; “reaction products” refers to products (i.e., what is obtained) from such a single reaction; “commercial products” refers to items manufactured or produced using reaction products as starting materials; “supported catalyst” and “catalyst” are

synonymous, and refer to a catalyst with a metal component over a support which can be an acidic oxide; “fatty acid” and “carboxylic acid” are synonymous; “fatty acid” is not included within the meaning of “hydrocarbon”; and cracking refers to a reaction that produces at least one hydrocarbon having a carbon chain shorter by at least three carbons than the fatty acid from which it was derived, and includes both primary and secondary cracking.

[00017] The products of the subject reactions according to multiple embodiments are suitable for use not only as direct drop-in fuels (e.g., motor gasoline, kerosene, diesel, aviation gasoline and aviation turbine fuel), but also as starting materials in the manufacture of a variety of commercial products, including but not limited to high viscosity lubricants, detergents, surfactants, solvents, and various petrochemicals, through methods which are known to persons of ordinary skill in the art.

BRIEF DESCRIPTION OF THE FIGURES

[00018] FIG. 1A shows a representative scanning electron microscope (SEM) image of SAPO-34 prepared using the process described herein.

[00019] FIG. 1B shows a representative SEM image of zeolite RHO prepared using the process described herein.

[00020] FIG. 1C shows a representative SEM image of DNL-6 prepared using the process described herein.

[00021] FIG. 1D shows a representative SEM image of hydrotalcite prepared using the process described herein.

[00022] FIG. 2A shows an X-Ray Diffraction (XRD) pattern of Pt/SAPO-34.

[00023] FIG. 2B shows an XRD pattern of Pt/hydrotalcite.

[00024] FIG. 2C shows an XRD pattern of Pt/RHO.

[00025] FIG. 2D shows an XRD pattern of Pt/DNL-6.

[00026] FIG. 3 is a bar graph showing selectivity for decarboxylation of oleic acid over catalysts prepared with potassium hexachlorplatinate solution (salt 1 according to Table I) at different reaction temperatures.

[00027] FIG. 4 is a bar graph showing selectivity for decarboxylation of oleic acid over catalysts prepared with tetraamine platinum nitrate solution (salt 2 according to Table I) at different reaction temperatures.

[00028] FIG. 5 is a plot of heptadecane selectivity as a function of temperature for decarboxylation of oleic acid over catalysts prepared with potassium hexachlorplatinate solution.

[00029] FIG. 6 is a plot of heptadecane selectivity as a function of temperature for decarboxylation of oleic acid over catalysts prepared with tetraamine platinum nitrate solution.

[00030] FIG. 7 is a plot showing the effect of temperature on the selectivity of the final products for deoxygenation of oleic acid over Pt/SAPO-34 prepared with potassium hexachlorplatinate solution.

[00031] FIGURES 8A and 8B show representative first and second transmission electron microscope (TEM) images of 5 % Pt/SAPO-34 catalyst prepared with potassium hexachlorplatinate solution.

[00032] FIGURES 8C and 8D show representative first and second TEM images of 5 % Pt/SAPO-34 catalyst prepared with tetraamine platinum nitrate solution.

[00033] FIG. 9A is a particle size distribution histogram of 5 % Pt/SAPO-34 catalyst prepared with potassium hexachloroplatinate solution.

[00034] FIG. 9B is a particle size distribution histogram of 5 % Pt/SAPO-34 catalyst prepared with tetraamine platinum nitrate solution.

[00035] Fig. 10 shows the total products distribution (% wt) for the decarboxylation of oleic acid at 325 and 245°C over four different catalysts prepared by two different salts, potassium hexachloroplatinate solution and tetraammine platinum nitrate solution, according to multiple embodiments and alternatives.

MULTIPLE EMBODIMENTS AND ALTERNATIVES

[00036] Embodiments of the present application are directed to reacting fatty acids over supported catalysts and further transformation of the straight-chain intermediate products of such reactions to form branched isomers of the straight-chain intermediates, aromatic and cyclic analogs of the straight-chain intermediates, and hydrocarbons having fewer carbons in their chain than the straight-chain intermediates as a result of cracking, wherein the final products formed through further transformation of the intermediate products are capable of being used in the manufacture of various products as described herein.

[00037] In some embodiments, a process for conducting a single catalytic reaction for the production of hydrocarbons from at least one fatty acid forming hydrocarbon reaction products comprises the steps of contacting fatty acids reactants with a supported catalyst, the catalyst comprising platinum over a support, the support being chosen from the group SAPO-34, SAPO-11, DNL-6, RHO, and hydrotalcite, and mixtures thereof; and isolating hydrocarbon reaction products.

embodiment, the fatty acids are decarboxylated and further transformed, over a multifunctional catalyst containing platinum over a support, to branched, cyclic and aromatic reaction products. In particular, hydrocracking can be advantageous for providing naphtha and other higher-value, lower molecular weight feedstocks obtained as reaction products.

[00041] Thus, in some embodiments the initially formed, straight-chain paraffin intermediates undergo further transformation to branched, cyclic and alkyl aromatic hydrocarbons. The decarboxylation and further transformation according to multiple embodiments also benefit from the influence of stronger acidic supports in further transforming the carbon skeleton of the linear C₁₆- C₁₈ paraffins (initial products of the decarboxylation of the fatty acid), by isomerization, aromatization, cracking, cyclisation, and hydrocracking. While these embodiments are not limited to fatty acids with 18 carbons, with C₁₈ fatty acids such as stearic acid and oleic acid, an increase of reaction temperature tends to increase the degree of decarboxylation and selectivity to C₁₇ paraffins and their derivatives obtained through further transformation. Higher selectivity to heptadecane and heptadecane-derivatives also occur in the presence of hydrogen. Dodecyl benzene is an example of further transformation of heptadecane to a C₁₇ aromatic. Dodecyl benzene is used in a number of commercial products, including as a starting material for detergents.

[00042] The process according to multiple embodiments and alternatives comprises contacting a feedstock having at least one fatty acid reactant of the chemical formula represented by R-COOH with a catalyst comprising at least one metal and at least one support chosen from the group SAPO-34, SAPO-11, DNL-6, RHO, and hydrotalcite. At least one product comprising one or more branched hydrocarbons is produced as part of a mixture, and such product contains one fewer carbons than the starting fatty acid reactant. In some embodiments, R contains at least six and no more than twenty-four carbon atoms. The

process further includes isolating the at least one product from other reaction products in the mixture. In certain embodiments, the at least one product is chosen from the group branched hydrocarbons, cyclic hydrocarbons and aromatic hydrocarbons.

[00043] In some embodiments, the at least one fatty acid reactant is a saturated fatty acid. Alternatively, the at least one fatty acid reactant is an unsaturated fatty acid. In the latter case, as part of the reaction process the at least one unsaturated fatty acid is optionally reduced to its saturated counterpart by hydrogenation, through methods known to persons of ordinary skill in the art.

[00044] In some embodiments, the at least one fatty acid reactant is obtained from a renewable feedstock of biological origin (i.e., biomass raw materials), such as, for example, plant oils; animal fats and oils; algae oils; waste vegetable oils; or oils from heterotrophic microbial organisms. Illustrative, non-limiting examples of heterotrophic microbial organisms are heterotrophic algae, oleaginous yeasts, and various bacteria. Optionally, the source of the at least one fatty acid consists of a mixture of two or more members of this group. Alternatively, the at least one fatty acid is obtained from an industrial or other non-biological source, such as, for example industrial greases, and waxes obtained from solid wastes, and paper mills. Optionally, the at least one fatty acid is a mixture of at least two fatty acids, each having 7-to-24 carbon atoms. In some embodiments, prior to the reaction and further transformation which are the subject of these descriptions, triglyceride esters are converted to fatty acids through methods known to persons of ordinary skill in the art such as hydrolysis, thermal hydrolysis, acid hydrolysis, among others.

[00045] In some embodiments, the renewable feedstock includes, but is not necessarily limited to, plant oils from a non-food oil crop such as jatropha oil, camelina oil, pennycress oil, pongamia oil, and carinata oil. Such non-food oil crops are generally less expensive to

produce or obtain, are more sustainable, and are significantly lower in greenhouse gas emissions than, for example, soy, rapeseed oil, or beef tallow. The use of such lower-cost, more sustainable oils with decarboxylation and further transformation processes as described herein, according to multiple embodiments and alternatives, provides increased production flexibility and cost-effectiveness for hydrocarbon fuels, chemicals, and other products described herein because production facilities can be distributed more evenly and in closer proximity to locations where these oil crops are grown.

[00046] In some embodiments, the at least one fatty acid reactant is diluted in a suitable solvent before commencing with decarboxylation to assist the flow of the fatty acid via a pump, among other purposes. As used herein, a suitable solvent would include hydrocarbons, such as, for example dodecane or hexadecane. In some embodiments, a mixture of two or more hydrocarbons is used as a solvent. In some embodiments, decarboxylation followed by further transformation of the linear hydrocarbon intermediate are carried out in a suitable solvent. Alternatively, a solvent-free reaction chamber is utilized.

[00047] If desired, such decarboxylation and further transformation, as described herein according to multiple embodiments and alternatives, are carried out in a reactor. In some embodiments, the reactor is a batch reactor. Alternatively, the reactor is a semi-batch reactor. Alternatively, the reactor is a continuous flow reactor. In certain embodiments, a single reactor is used for both decarboxylation and further transformation (as well as hydrogenation of unsaturated fatty acids, as desired) over the catalysts described herein.

[00048] Optionally, the at least one fatty acid reactant is passed over a catalyst of this invention in a reaction zone contained within the reactor. In some embodiments, the reactions are carried out at a temperature in a range of 200°C – 450°C (temperatures are understood to be in Celsius unless otherwise noted). Alternatively, the temperature is in a

range of 245°C – 325°C. In some embodiments, decarboxylation is carried out at a pressure in a range of 1 bar – 60 bar, preferably about 20 bar.

[00049] Generally, it will be appreciated that the degree of decarboxylation of the at least one fatty acid reactant and selectivity to the primary intermediate are influenced by factors such as the reaction temperature and the type of catalyst (both the type of support and the type of platinum salt used for impregnation of the support). Higher temperatures tend to increase the degree of decarboxylation (~98% in some cases, as discussed below) and selectivity to heptadecane (up to ~66%), and the use of more acidic supports such as SAPO-34 tend to increase the degree of decarboxylation and the selectivity to heptadecane, in addition to the selectivity to dodecylbenzene.

Preparation and Characterization of the Supported Catalysts

[00050] In certain embodiments, deoxygenation and further transformations are accomplished in a single step process over a supported catalyst chosen from the group: Pt/SAPO-34, Pt/DNL-6, Pt/Rho and Pt/hydrotalcite.

[00051] SAPO-34 is a silicoaluminophosphate zeolite having composition $\text{Si}_x\text{Al}_y\text{P}_z\text{O}_2$, where $x = 0.01\text{-}0.98$, $y = 0.01\text{-}0.60$, and $z = 0.01\text{-}0.52$ with ~0.38 nanometer (nm) unimodal micropores. In an example embodiment, preparation of this support was according to teachings and methods described by Szostak, R.; Molecular Sieves: Principles of Synthesis and Identification, Van Nostrand Reinhold, New York (1989), in which an aluminum source such as 99.9% $\text{Al}(\text{i-C}_3\text{H}_7\text{O})_3$, phosphoric acid (H_3PO_4) and deionized water are stirred for 3 hours to form a homogenous solution. Ludox AS-40 colloidal silica (40 wt% suspension in water Sigma-Aldrich) is then added, and the resulting solution is stirred for 3 hours. Then, tetraethyl ammonium hydroxide (35 wt% solution in water Sigma-Aldrich), dipropylamine (99%, Aldrich) and cyclohexylamine (99% Sigma-Aldrich) are added, and this solution was

stirred for 4 days at 60°C. The resulting solution is then transferred into a stainless-steel autoclave and held at 220 °C for 24 hours, and after appropriate cooling the solid product is separated by centrifuge and washed a sufficient number of times with deionized water. Finally, SAPO-34 is dried and then calcined at 550°C for 5 hours (the calcination heating and cooling rates were 1 and 2 °C/min, respectively). Alternatively, SAPO-11 is prepared in the same way for use as the support instead of SAPO-34.

[00052] The scope of the embodiments provided herein is not limited to the method chosen for preparing the supported catalyst. Rather, multiple alternatives exist for preparing the supported catalyst as are known to skilled artisans, e.g., impregnation, deposition-precipitation, ion-exchange, and adsorption.

[00053] FIG. 1A shows a representative scanning electron microscope (SEM) image of SAPO-34 showing cubic like morphology with average size in the range of 2.3 micrometers (μm). FIG. 2A shows the XRD pattern of Pt/SAPO-34, which corresponds to chabazite structure, typical of SAPO-34. From this, it is reasonably concluded that the incorporation of Pt did not modify the structure of SAPO-34. Similar results and conclusions were reached for the other catalysts when the XRD of the typical support was compared with the impregnated support with pt.

[00054] DNL-6 is a silicoaluminophosphate molecular sieve with the RHO framework having pore size of ~0.36 nm. Preparation of this support was according to teachings and methods described by Su, X., Tian, P., Li, J., Zhang, Y., Meng, S., He, Y., Fan, D., Liu, Z., *Microporous and Mesoporous Materials* (2011) 113-119, 144, in which under consistent stirring, 1.17g orthophosphoric acid (85 wt%) and 0.625g tetraethyl orthosilicate were mixed with a solution of 3.06g aluminium isopropoxide and 13.5g deionized water, and then an aqueous solution of cetyltrimethylammonium bromide (CTAB) was added with final addition

of 1.097g of DEA (diethylaniline) template. The specific gel composition for the hydrothermal synthesis was: Al: P: Si: DEA: CTAB: H₂O= 1: 0.8: 0.2: 1: 0.1: 50. The final gel mixture was transferred into a stainless-steel autoclave and held at 200°C for 24 hours, after which the autoclave was cooled and the solid product was collected by centrifuge, washed three times with deionized water, and dried at 110°C overnight. Calcination was carried out at 600 °C for 4 hours to remove organic species (the calcination heating and cooling rates to remove organic species were 1 and 2 °C/min, respectively).

[00055] FIG. 1B shows a representative SEM image of zeolite RHO prepared using the process described herein, and showing spherical morphology with size in the range of 1.5 µm. FIG. 2D shows the XRD pattern of Pt/DNL-6.

[00056] Zeolite RHO comprises a body-centered cubic arrangement of Linde Type A (LTA) framework cages displaying an average pore size of ~0.36 nm. Preparation of this support was according to teachings and methods described by Chatelain, T., Patarin, J.; Farre, R.; Petigny, O.; Schulz, P.; Zeolites, (1996) 17, 328; and Palomino, M.; Corma, A.; Jorda, J.L.; Rey, F.; Valencia, S., Chemical Communications 2012, 48, 215, in which 0.94 g of crown ether 18-C-6; 0.705 g of caesium hydroxide and 0.34 g of sodium hydroxide were dissolved in 6.04 g of distilled water. 1.32 g of sodium aluminate were then added to the above solution, and the resulting mixture was stirred until a clear solution was formed. Subsequently, 10.5 g of colloidal silica (Ludox AS-40) were added, and the resulting reaction mixture was stirred at room temperature for 24 hours. The final gel composition was: 1.8 Na₂O : 0.3 Cs₂O : Al₂O₃ : 10 SiO₂ : 0.5 R : 100 H₂O (where R is the crown ether 18-C-6). Zeolite crystallization was carried out in an autoclave at 150° for 1 day. The zeolite RHO was recovered after filtration, washing with water and drying at 100° overnight. It was then

calcined at 500 °C for 3 hours to remove organic species (the calcination heating and cooling rates to remove organic species were 1 and 2 °C/min, respectively).

[00057] FIG. 1C shows a representative SEM image of DNL-6 prepared using the process described herein, and showing cubic-like morphology with average size in the range of 2.7 μm . FIG. 2C shows the XRD pattern of Pt/RHO.

[00058] Hydrotalcite was synthesized according to teachings and methods described by Erickson, et al., Journal of Thermal Analysis and Calorimetry (2005); 82(3): 603-608. In a typical synthesis, 200 ml solution containing 0.126 M $\text{Zn}(\text{NO}_3)_2$ and 0.063M $\text{Al}(\text{NO}_3)_3$ was prepared. The solution was stirred and heated at 85°C, then a stoichiometric amount of urea was added and the solutions was kept under reflux for 24 hours, then filtered and washed with boiling water several times.

[00059] FIG. 1D shows a representative SEM image of hydrotalcite prepared using the process described herein, and showing irregular agglomerated morphology with size in the range of 2.7 μm containing needle shapes. FIG. 2B shows the XRD pattern of Pt/hydrotalcite.

[00060] For each support, i.e., SAPO-34, DNL-6, Zeolite Rho, and hydrotalcite, a 5% (wt) pt/support catalyst was prepared by impregnation of the support with two different salts of platinum (potassium hexachlorplatinate and tetraammine platinum nitrate, respectively). 0.126 g of Pt source (salt 1 or salt 2) was dissolved in de-ionized water (0.7 cm^3/g -support) and then impregnated over the support meanwhile the suspension was stirred. The mixture was further dried overnight at 100°C followed by calcination at 400°C for 5 hours, followed by reduction in flowing hydrogen at 450°C for 2hr to remove the ligands of the precursor and to reduce the metal to its active elemental state.

[00061] The 5% by weight ratio of metal to support the examples describe is not meant to be limiting. The ratio generally varies between 0.2-10% catalyst-support by weight. In some embodiments, the metal-to-support ratio is about 3 – 5% by weight.

[00062] The catalysts were characterized by X-ray diffraction (XRD), nitrogen adsorption (BET), transmission electron microscopy (TEM) and scanning electron microscopy (SEM). XRD patterns were collected on a Bruker D8 Discover diffractometer at 40 kilovolts (kV) and 40 milliamps (mA) with Cu K α radiation. BET surface areas and N₂ adsorption-desorption isotherms were collected in a Micromeritics Tristar-3000 porosimeter at 77 K using liquid nitrogen as coolant. Before measurements, each catalyst was degassed at 150 °C for 3 hours. Transmission electron microscopy (TEM) was used to inspect the morphology of catalysts. TEM images were taken on Technai F20 FEI TEM using a field emission gun, operating with an accelerating voltage of 200kV. The scanning electron microscopy (SEM) was performed on a FE-SEM (FEI Nova 600), with an acceleration voltage of 6 kV.

[00063] Surface areas of the SAPO-34, DNL-6, and hydrotalcite supports with and without platinum are listed in Table I:

Table I – Surface area of supports with and without addition of Pt

Sample	BET Surface area (m²/g)
SAPO-34	490.4
Pt/SAPO-34 (salt1)	406.4
Pt/SAPO-34 (salt2)	478.2
DNL-6	400
Pt/DNL-6 (salt1)	250

Pt/DNL-6 (salt2)	280
Hydrotalcite	55
Pt/Hydrotalcite (salt1)	49
Pt/Hydrotalcite (salt2)	53

[00064] According to Table 1, the surface area of the supports did not significantly decrease after adding platinum from either of the platinum sources (i.e., salt 1, potassium hexachloroplatinate and salt 2, tetraammine platinum nitrate). For example, the surface area of SAPO-34 was 490.4 m²/g and the surface area of Pt/SAPO-34 for salt 1 and 2 were 406.4 and 478.2 m²/g, respectively. However, it can be seen that the surface area of the catalysts prepared by salt 2 is a little more than those which are prepared by salt 1.

[00065] In certain embodiments, the catalyst is capable of being re-used multiple times without substantial changes in the performance, and without substantial changes to physicochemical properties such as acidity, surface area and pore size distribution, albeit this is not meant to imply that the number of re-uses is unlimited.

Reaction Procedure

[00066] The following non-limiting examples relate to the decarboxylation and further transformation of oleic acid, and are offered to further illustrate various embodiments according to the teachings herein. However, it is to be understood that these are illustrative only and not to be construed as limiting the scope of the subject matter described and claimed herein.

[00067] In the examples described herein, oleic acid (90%, Alfa-Aesar) was used as the unsaturated fatty acid. Catalyst was pre-activated in the oven for 3 hours at 150°C. The decarboxylation reactions were conducted in a 250 mL stainless steel, high pressure

autoclave reactor (Parr model 4576A). For each catalyst in Table I, oleic acid and the catalyst were loaded into the reactor with a mass ratio of 20:1. Before starting the reaction, the reactor was flushed with H₂ and the pressure was increased to the desired reaction pressure (20 bar). Under constant stirring conditions, the reactor was heated at a rate of 10°C/min to the reaction temperature (245 and 325°C, respectively). After the reaction, the catalyst was separated, by filtration, from the liquid product and washed with acetone for further characterization. While this example is provided to illustrate the reaction procedure, conditions, and products, it will be appreciated by skilled artisans that embodiments of the present invention include those in which any source obtained from a renewable feedstock of biological origin as described above and containing at least one fatty acid is used in the reaction procedure as described.

[00068] For example, non-limiting examples of fatty acid constituents which can be derived from such feedstock include unsaturated fatty acids comprising:

[00069] myristoleic acid (chemical structure $\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$);

[00070] palmitoleic acid ($\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$);

[00071] sapienic acid ($\text{CH}_3(\text{CH}_2)_8\text{CH}=\text{CH}(\text{CH}_2)_4\text{COOH}$);

[00072] oleic acid ($\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$);

[00073] elaidic acid ($\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$);

[00074] vaccenic acid ($\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}(\text{CH}_2)_9\text{COOH}$);

[00075] linoleic acid ($\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$);

[00076] linoelaidic acid ($\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$);

[00077] α -linolenic acid ($\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$);

[00078] arachidonic acid

($\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_3\text{COOH}$);

[00079] eicosapentaenoic acid

($\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_3\text{COOH}$); and

[00080] erucic acid ($\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_{11}\text{COOH}$),

[00081] as well as saturated fatty acids comprising:

[00082] caprylic acid ($\text{CH}_3(\text{CH}_2)_6\text{COOH}$);

[00083] capric acid ($\text{CH}_3(\text{CH}_2)_8\text{COOH}$);

[00084] lauric acid ($\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$);

[00085] myristic acid ($\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$);

[00086] palmitic acid ($\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$);

[00087] stearic acid ($\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$);

[00088] arachidic acid ($\text{CH}_3(\text{CH}_2)_{18}\text{COOH}$);

[00089] behenic acid ($\text{CH}_3(\text{CH}_2)_{20}\text{COOH}$); and

[00090] lignoceric acid ($\text{CH}_3(\text{CH}_2)_{22}\text{COOH}$),

[00091] and mixtures thereof.

[00092] In certain embodiments, the reaction procedure further comprises hydrogenating one or more unsaturated fatty acids to their saturated analogs, e.g., oleic acid

to stearic acid and palmitoleic acid to palmitic acid. Further, in the reaction, decarboxylation produces a hydrocarbon intermediate having one fewer carbons than a given reactant. Non-limiting examples include heptadecane as an intermediate in the reaction of oleic acid and pentadecane in the reaction of palmitoleic acid.

Experimental Results and Product Analysis

[00093] With respect to the above-mentioned examples, for each reaction the liquid phase product was withdrawn from the reactor and analyzed with a gas chromatograph (GC, 7820 A) equipped with a HP-5 MS column (with dimensions of 30 m $\times$ 250 μ m $\times$ 0.25 μ m) and a 5975 MSD detector. Samples were silylated with *N,O*-bis (trimethyl)-trifluoroacetamide, BSTFA (Acros organics, 98%) in preparation for analysis by GC. After addition of silylation agent, the samples were kept at 60°C for 1 hour. A sample of 0.2 μ L was injected into the GC column (225°C, 10.5 psi) with a split ratio 20:1, and the carrier gas (helium) flow rate was 1 mL/min.²² The following temperature program of the gas chromatograph was used for analysis: 100°C for 5 min, 300°C (20°C/min, for 2 min). Quantitative analysis was accomplished by generating and using calibration curves for each compound of interest. The product identification was confirmed with a gas chromatograph - mass spectrometer (GC-MS). Generally, the analysis of the results focused on the roles of the support, the platinum source, and reaction temperature on the decarboxylation and further transformation of the fatty acids.

[00094] The amount of fatty acid groups remaining in the products after the reaction was evaluated by quantifying the acid number. Acid number is the mass of potassium hydroxide in milligrams that is required to neutralize one gram of chemical substance. To quantify the acid number, a known amount of sample (about 0.1g) is dissolved in a solvent

(ethanol + Petroleum ether), then titrated with a solution of sodium hydroxide (NaOH, 0.1N) using phenolphthalein as a color indicator.

[00095] The acid number is calculated from this equation:

[00096] Acid number = $56.1 \times NV/W$, where

[00097] $N = 0.1$ (N)

[00098] V = volume of NaOH consumed (ml)

[00099] W = mass of the sample (g)

[00100] The decarboxylation % was calculated using the acid number of oleic acid and acid number of the product using the following relation:

[00101] % Decarboxylation = $(\text{acid number of oleic acid} - \text{acid number of the product}) / \text{acid number of oleic acid} \times 100\%$

[00102] Tables II and III show the acid number of the reaction products (indicative of the concentration of unconverted fatty acid) over all these catalysts in the case of each of two used to impregnate the supports. In each case, the acid number was lower at 325°C compared to 245°C:

Table II. Acid numbers of decarboxylation product of oleic acid over catalysts

prepared by salt 1 (potassium hexachlorplatinate) at 245 and 325°C

	Pt/DNI-6		Pt/RHO		Pt/SAPO-34		Pt/Hydrotalcite	
T (°C)	325	245	325	245	325	245	325	245
Acidity	4.9	37.6	9.7	19.3	6.6	33.9	4.0	19.8

Table III. Acid numbers of decarboxylation product of oleic acid over catalysts

prepared by salt 2 (tetraammine platinum nitrate) at 245 and 325°C

	Pt/DNI-6		Pt/RHO		Pt/SAPO-34		Pt/Hydrotalcite	
T (°C)	325.0	245.0	325.0	245.0	325.0	245.0	325.0	245.0
Acidity	2.87	17	30.0	34.0	2.9	16.8	2.1	17.5

[000103] The primary intermediate in the reaction was stearic acid formed by hydrogenation of oleic acid, which then underwent decarboxylation to form heptadecane and/or derivatives including branched paraffins formed by isomerization of heptadecane. Other intermediates included various fatty acids, such as nonanoic acid, decanoic acid and undecanoic acid formed through hydrogenation of unsaturated fatty acids having the same number of carbons. Upon completion of the reaction, besides heptadecane the other components in the liquid product included branched paraffins formed by isomerization of the heptadecane, aromatics formed by cyclisation and aromatization (e.g., dodecyl benzene) and lower molecular weight hydrocarbons (mostly C₆-C₁₆ paraffins) formed by cracking of the heptadecane. No oleic acid was observed in the products under all reaction conditions, suggesting 100% or near 100% conversion of oleic acid. The amount of stearic acid and other fatty acids in the product was lower at 325°C compared to 245°C for the all catalysts which confirms that a higher degree of decarboxylation was observed at 325°C. Some alkenes such as undecene, dodecene, tridecene, tetradecene, hexadecene, heptadecene and octadecene were also observed in the products.

[000104] Fig. 10 provides a more detailed distribution according to mass balance of the liquid products formed in the reactions for all the conditions (two temperatures, two sources of platinum used in forming each of four catalysts). Other gases like methane, butane and propane, as well as carbon dioxide, were present in the gas stream of the products. The column in Fig. 10 with the heading % gas represents condensed material from the gas stream. Products in the gas phase were thus included on a pro rata basis with the liquid portion that was analyzed in calculating the weight percentages. The selectivity to heptadecane was highest over Pt/SAPO-34, which also demonstrated the highest selectivity to dodecylbenzene.

This can be explained by the difference in acidity of the supports, given that a support such as RHO has lower-pH strong acid sites and higher-pH weak acid sites compared to SAPO-34.

[000105] Fig. 3 plots the decarboxylation of 40 milliliters (mL) of oleic acid over different catalysts (2 g of catalyst for 2 hr at a pressure of 20 bar) as a function of temperature (245 and 325°C) when potassium hexachloroplatinate solution was used to incorporate Pt on the supports. For reactions over all four catalysts (Pt/DNL-6, Pt/RHO, Pt/SAPO-34, and Pt/hydrotalcite) a higher degree of decarboxylation was observed at 325°C than at 245°C. The same pattern was observed under the same reactions conditions when the supports were impregnated with tetraammine platinum nitrate solution (Fig. 4).

[000106] Fig. 5 and Fig. 6 show the effect of reaction temperature and catalyst on selectivity to heptadecane, the linear C₁₇ paraffin obtained by the decarboxylation of oleic acid. Heptadecane selectivity increased with temperature, and was highest in the presence of Pt-SAPO-34. Fig. 5 represents the catalyst wherein potassium hexachloroplatinate solution was used to incorporate Pt on the supports. Fig. 6 represents the catalyst wherein tetraammine platinum nitrate solution was used to incorporate Pt on the supports.

[000107] Similarly, Fig. 7 shows the effect of reaction temperature in a range of 250°C–325°C, concerning selectivity of the final products in the catalytic deoxygenation of oleic acid over Pt/SAPO-34, for the catalyst wherein tetraammine platinum nitrate solution was used to incorporate Pt on the supports. As expected on thermodynamic grounds, selectivity to normal paraffins, e.g., heptadecane, increased with temperature and selectivity to other alkane products (C₆–C₁₆, C₁₈ and C₁₉) decreased with temperature. In addition, a heptadecane selectivity of 66.9% and dodecylbenzene selectivity of 7.5% were observed after 2 hr in the presence of H₂ at 325 °C over Pt/SAPO-34.

[000108] For Pt/SAPO-34, Pt/SAPO-11, Pt/DNL-6, Pt/Rho, and Pt/hydrotalcite, a higher degree of decarboxylation and a higher selectivity to heptadecane were observed over the catalysts prepared with tetraammine platinum nitrate solution. For example, for the reaction at 325 °C, decarboxylation over Pt/SAPO-34 prepared by impregnation with tetraammine platinum nitrate solution was higher compared to the catalyst prepared by potassium hexachloroplatinate solution (98.5% and 96.7%, respectively, compare Fig. 3 and 4). Moreover, heptadecane selectivity over Pt/SAPO-34 prepared by impregnation with tetraammine platinum nitrate solution was higher compared to the catalyst prepared by impregnation with potassium hexachloroplatinate solution (66.9% and 29.4%, respectively, compare Fig. 5 and 6).

[000109] In addition to what is shown for Pt/SAPO-34, Pt/DNL-6, Pt/Rho, and Pt/hydrotalcite in the figures, for the reaction over Pt/SAPO-11 at 325°C, the liquid reaction products are shown below (with the % gas represented in the products being 9.4%):

hexane	1.8% (by weight)
heptane	2.4%
octane	2.9%
nonane	2.4%
decane	2.4%
undecane	2.4%
dodecane	2.9%
tridecane	2.9%

tetradecane	3.5%
pentadecane	2.9%
hexadecane	3.5%
heptadecane	40.4%
octadecane	2.4%
nanodecane	2.9%
dodecylbenzene	14.1%
stearic acid	0.8%

[000110] Fig. 8A and 8B show representative TEM images of the Pt/SAPO-34 catalysts employed in this study. In particular, a higher density of well-dispersed and smaller platinum nanoparticles on SAPO-34 support were observed when tetraammine platinum nitrate solution was used as a Pt source (Fig. 8B) as compared to potassium hexachloroplatinate solution (Fig. 8A). In general, the Pt particle histogram of Fig. 9 for the catalyst formed with tetraammine platinum nitrate solution shows a slightly higher fraction of small nanoparticles (in the 1-3 nm range) to that of catalyst formed with potassium hexachloroplatinate solution. Although both are suitable sources, a higher degree of decarboxylation and higher selectivity to heptadecane was observed with tetraammine platinum nitrate as the platinum source, largely because the catalysts prepared by this salt exhibit more uniform and well dispersed platinum nanoparticles compared to catalysts prepared with potassium hexachloroplatinate solution.

Reaction Products and Examples of Commercial Uses

[000111] The above examples are not meant to limit the scope of the embodiments described and/or claimed herein. Rather, it will be appreciated that a multiplicity of reaction products are generated from a given source feedstock. Considering that a plurality of fatty acids are derived from feedstocks obtained from natural and industrial sources, the number of possible reaction products is further increased. Non-limiting examples of final products of the reactions according to multiple embodiments and alternatives include methyl-, ethyl-, propyl, or butyl-substituted isomers of alkanes, which are shorter than the straight-chain intermediates. For example, 2-methylheptadecane, 8-methylheptadecane, 2-ethylpentadecane, 2-propyltetradecane, 2-butyltridecane, and 2-methyl dodecane are examples of alkyl-substituted isomer reaction products of stearic acid, with heptadecane serving as the straight-chain intermediate. Dodecyl benzene and undecylbenzene (abbreviated UDB in Figure 10) are examples of aromatic products. Non-limiting examples of cyclic products include 1,2-dipropylcyclopentane and 1-undecanecyclopentane.

[000112] In certain embodiments, the paraffinic reaction products of decarboxylation and further transformation (e.g., isomerization) of the fatty acid reactants are useful as aviation turbine fuel, which meets the specifications of ASTM D1655 and/or ASTM D7566, the standards for Jet-A aviation turbine fuel. One of the key specifications of these standards is the boiling point range of 180°C-300°C, which can be achieved with the correct balance of cracking and isomerization. The process for the production of these hydrocarbons, as described herein according to multiple embodiments and alternatives, can be tuned as selectably desired by a user to achieve the same boiling point range and other specifications using different feedstock sources with different carbon chain length distributions and varying degrees of cracking or branching.

[000113] In certain embodiments, the paraffinic reaction products of decarboxylation and further transformation of the fatty acid reactants (i.e., reaction products) are useful as a high-octane motor gasoline meeting the specifications of ASTM D4814-11B, including a boiling point range of about 35°C-200°C, and these products will also have an octane rating greater than about 90. The process described herein allows for higher-octane gasoline because it can be tuned to convert the (linear) fatty acid starting materials preferentially into specific branched, cyclic and aromatic hydrocarbons, with a minimum of side reactions. For example, branched paraffinic hydrocarbons have higher octane values than multi cyclic paraffinic hydrocarbons. By way of non-limiting illustration, a C9 naphthene has an octane rating of approximately 35, whereas a C12 branched paraffin has an octane rating of approximately 85, yet both molecules have boiling points within about 5°C – 10°C of one another. For practical purposes, petroleum naturally contains many different species, making it economically impractical, if not impossible, for petroleum refineries to separate hydrocarbons with better anti-knock characteristics (higher octane) from those with poorer anti-knock characteristics (lower octane) when they are of the same or similar molecular weight or boiling points. Consequently, products obtained from fatty acids according to multiple embodiments and alternatives disclosed herein produce higher-octane gasoline with lower conversion and separation costs than petroleum refineries typically can achieve.

[000114] In certain embodiments, the reaction products are useful as aviation gasoline after the addition of monocyclic aromatics, such as benzene, toluene, and xylene, which can be used to increase the octane to 100 or more. One advantage of this process for producing aviation gas is that the branched hydrocarbon reaction products resulting from decarboxylation and further transformation in a single step according to present embodiments have a significantly higher starting octane, as described above, before the addition of any aromatics or tetraethyl lead, than paraffinic hydrocarbons obtained from petroleum.

Consequently, certain aviation gasoline specifications (e.g., ASTM D7719) requiring an octane rating of 100 and a boiling point range of 20° -175° can be satisfied without the addition of tetraethyl lead, which is prohibited by ASTM D7719 (the standard for lead-free test aviation gas), and with the addition of lesser amounts or no amounts of aromatics. Likewise, the specifications of D910 (the standard for leaded aviation gas) can be met with the addition of lesser amounts of lead and with lesser amounts or no amounts of aromatics. In particular, it is possible to meet the D910 specifications for Grade 100 Low Lead (LL) and Grade 100 Very Low Lead (VLL) aviation gas, which limit tetraethyl lead content to 0.53 and 0.43 mL/L of fuel, respectively. Advantageously, this reduces the cost of adding tetraethyl lead or aromatics to aviation gas.

[000115] In certain embodiments, the reaction products can be used as feedstocks for downstream processes to produce mid-chain (between 9 and 18 carbons) or long-chain (greater than 20 carbons) chlorinated paraffins. Alternatively, they can be used as feedstocks for downstream processes to produce alpha olefins and poly alpha olefins; the appropriate carbon chain lengths of paraffinic hydrocarbons for this application would be between 9-18 carbons. Surfactants are compounds that reduce the surface tension between liquid- liquid and liquid- solid phases and are used as detergents, dispersants and emulsifiers. Alpha olefin sulfonates (AOS) and linear alkyl benzenes (LAB) are typical examples of detergents that are made from linear hydrocarbons containing 9 to 18 carbon atoms. In current practice, these linear paraffins are obtained by separation from petroleum fractions, like kerosene, using molecular sieves. In one embodiment of the present invention, these linear hydrocarbons are obtained from fatty acids derived from renewable, biological sources such as those described hereinabove. Accordingly, it will be appreciated that the ability to obtain linear olefin reaction products according to present embodiments is advantageous. For example, there are no known practical alternatives as starting materials for the production of commercial AOS

aside from linear olefins. In this regard, the present embodiments offer advantages and benefits compared to obtaining them by separation from petroleum fractions.

[000116] In certain embodiments, the reaction products can be used as aliphatic solvents for environmentally friendly cleaning fluids. These solvents may offer improved health and safety conditions during use in the workplace and elsewhere given the significantly lower levels of volatile organic compounds (“VOCs”) and of aromatics, while still meeting other key specifications for degreasing solvents and cleaning fluids, such as flash point and drying time. In still other embodiments, the paraffinic hydrocarbons produced from decarboxylation and isomerization meet the specifications of MIL-PRF-32295, such as flash point above about 140° F; vapor pressure <0.5 mm Hg at 20° C; specific gravity between 0.950-0.960; VOC Content <25 grams/liter; and distillation range within approximately 185 - 205° C. MIL-PRF-32295 is the military specification for environmentally friendly cleaning fluids, which is now being required in order to protect workers’ health and safety.

[000117] In certain embodiments where decarboxylation is followed by further transformation involving hydrocracking, olefinic hydrocarbons are produced, and such reaction products can be used as base stock for lubricants. For example, mid-chain olefins with internal double bonds can be used as base stock for lubricants with desired levels of viscosity index, lubricity, and oxidative stability.

[000118] In certain embodiments, the reaction products are capable of being distinguished from hydrocarbons produced by petroleum refineries or by hydrodeoxygenation of triglycerides. For example, in many embodiments, the products obtained by the process of the present invention are expected to be very low in sulfur, are expected to significantly exceed the Ultra Low Sulfur Diesel (ULSD) specification of no more than 15 ppm sulfur, and actually are expected to have less than about 5 ppm sulfur. It is also possible to distinguish

the reaction products of the present embodiments from those of paraffinic hydrocarbons produced using conventional techniques at a petroleum refinery based on the ratio of radioactive isotope Carbon-14 to Carbon-12. Specifically, this ratio is expected to be higher for products obtained by processes according to embodiments and alternatives described herein, than for the same products obtained from petroleum. Accordingly, testing methods regarding the ratio of Carbon-14 to Carbon-12 could be used to determine if particular paraffinic hydrocarbons came from renewable feedstocks according to multiple embodiments and alternatives, or whether they came from petroleum sources. Typically, the Carbon-14 to Carbon-12 ratio in contemporary carbon sources, such as renewable triglycerides, is about 10^{-12} , whereas the Carbon-14 to Carbon-12 ratio in fossil fuels such as petroleum (or hydrocarbons derived from petroleum) is 100 times lower, at a value of about 10^{-14} . Accordingly, testing methods regarding the ratio of Carbon-14 to Carbon-12 could be used to determine if particular paraffinic hydrocarbons came from renewable feedstocks according to multiple embodiments and alternatives, or whether they came from petroleum sources.

[000119] It will be understood that the embodiments described herein are not limited in their application to the details of the teachings and descriptions set forth, or as illustrated in the accompanying figures. Rather, it will be understood that the present embodiments and alternatives, as described and claimed herein, are capable of being practiced or carried out in various ways. Also, it is to be understood that words and phrases used herein are for the purpose of description and should not be regarded as limiting. The use herein of such words and phrases as “including,” “such as,” “comprising,” “e.g.,” “containing,” or “having” and variations of those words is meant to encompass the items listed thereafter, and equivalents of those, as well as additional items.

Accordingly, the foregoing descriptions of several embodiments and alternatives are meant to illustrate, rather than to serve as limits on the scope of what has been disclosed herein. The descriptions herein are not intended to be exhaustive, nor are they meant to limit the understanding of the embodiments to the precise forms disclosed. It will be understood by those having ordinary skill in the art that modifications and variations of these embodiments are reasonably possible in light of the above teachings and descriptions.

CLAIMS

What is claimed is:

1. A process for conducting a single catalytic reaction for the production of hydrocarbons from at least one fatty acid forming hydrocarbon reaction products, comprising the steps of:

contacting fatty acids reactants with a supported catalyst, the catalyst comprising a platinum metal component over a support, the support being chosen from the group SAPO-34, SAPO-11, DNL-6, RHO, and hydrotalcite, and mixtures thereof; and

isolating hydrocarbon reaction products;

wherein the metal comprises about 1% to about 10 % by weight of the catalyst, and the surface area of the support is between about 50 m²/g and about 490 m²/g.

2. The process of claim 1, wherein the metal comprises about 3% to about 5 % by weight of the catalyst.

3. The process of claim 1, wherein decarboxylation and cracking both occur during the catalytic reaction to yield at least one reaction product having a carbon chain shorter by at least three carbons than the fatty acid from which it was derived.

4. The process of claim 1, wherein decarboxylation and conversion both occur during the catalytic reaction to yield at least one branched reaction product.

5. The process of claim 1, wherein decarboxylation and conversion both occur during the catalytic reaction to yield at least one cyclic reaction product.

6. The process of claim 2, wherein at least one fatty acid is unsaturated, and decarboxylation and conversion both occur during the catalytic reaction to yield at least one aromatic reaction product.

7. The process of claim 1, carried out at a reaction temperature between about 200°C and about 450°C.

8. The process of claim 7, carried out at a reaction temperature no greater than about 325°C.

9. The process of claim 1, wherein the at least one fatty acid has between about 7 and 24 carbons.

10. The process of claim 2, wherein at least about 80% of fatty acids are converted to hydrocarbon reaction products.

11. The process of claim 2, wherein at least about 95% of fatty acids are converted to hydrocarbon reaction products.

12. The process of claim 1, wherein the at least one fatty acid is obtained from a renewable source chosen from the group plant oils; animal fats, animal oils; algae oils; waste vegetable oils; and oils from heterotrophic microbes, and mixtures thereof.

13. The process of claim 12, wherein the plant oil is chosen from the group jatropha oil, camelina oil, pennycress oil, pongamia oil, and carinata oil, and mixtures thereof.

14. A process for generating a feedstock, comprising the steps of:

contacting fatty acids reactants with a supported catalyst, the catalyst comprising a platinum metal component over a support, the support being chosen from the group SAPO-34, SAPO-11, DNL-6, RHO, and hydrotalcite, and mixtures thereof; and

isolating hydrocarbon reaction products,

wherein the metal comprises about 1% to about 10% by weight of the catalyst, and the surface area of the support is between about 50 m²/g and about 490 m²/g; and

wherein decarboxylation and conversion both occur during the catalytic reaction to yield at least one reaction product chosen from the group branched hydrocarbon reaction product, cyclic hydrocarbon reaction product, and aromatic hydrocarbon reaction product.

15. The process of claim 14, wherein the metal comprises about 3% to about 5% by weight of the catalyst.

16. The process of claim 15, wherein the feedstock is suitable for the manufacture of at least one commercial product, and the at least one commercial product is chosen from the group: gasoline having an octane rating greater than about 85; aviation fuel meeting the standard set forth in ASTM D1655; cleaning fluid having a flash point above about 140° F and VOC Content <25 grams/liter; AOS detergent having between 9 and 18 carbons; and LAB detergent having between 9 and 18 carbons; lubricant; surfactant, and solvent.

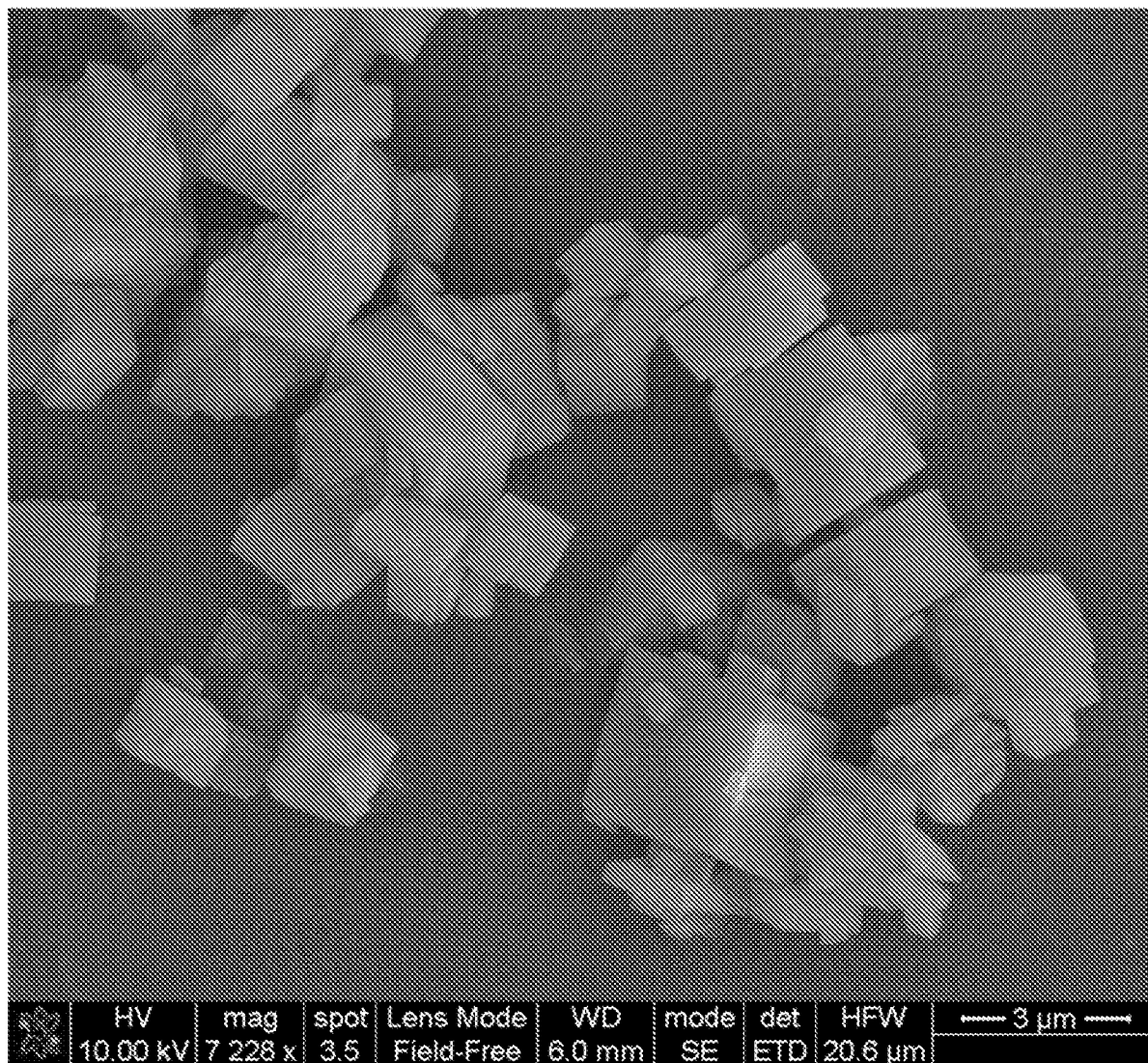
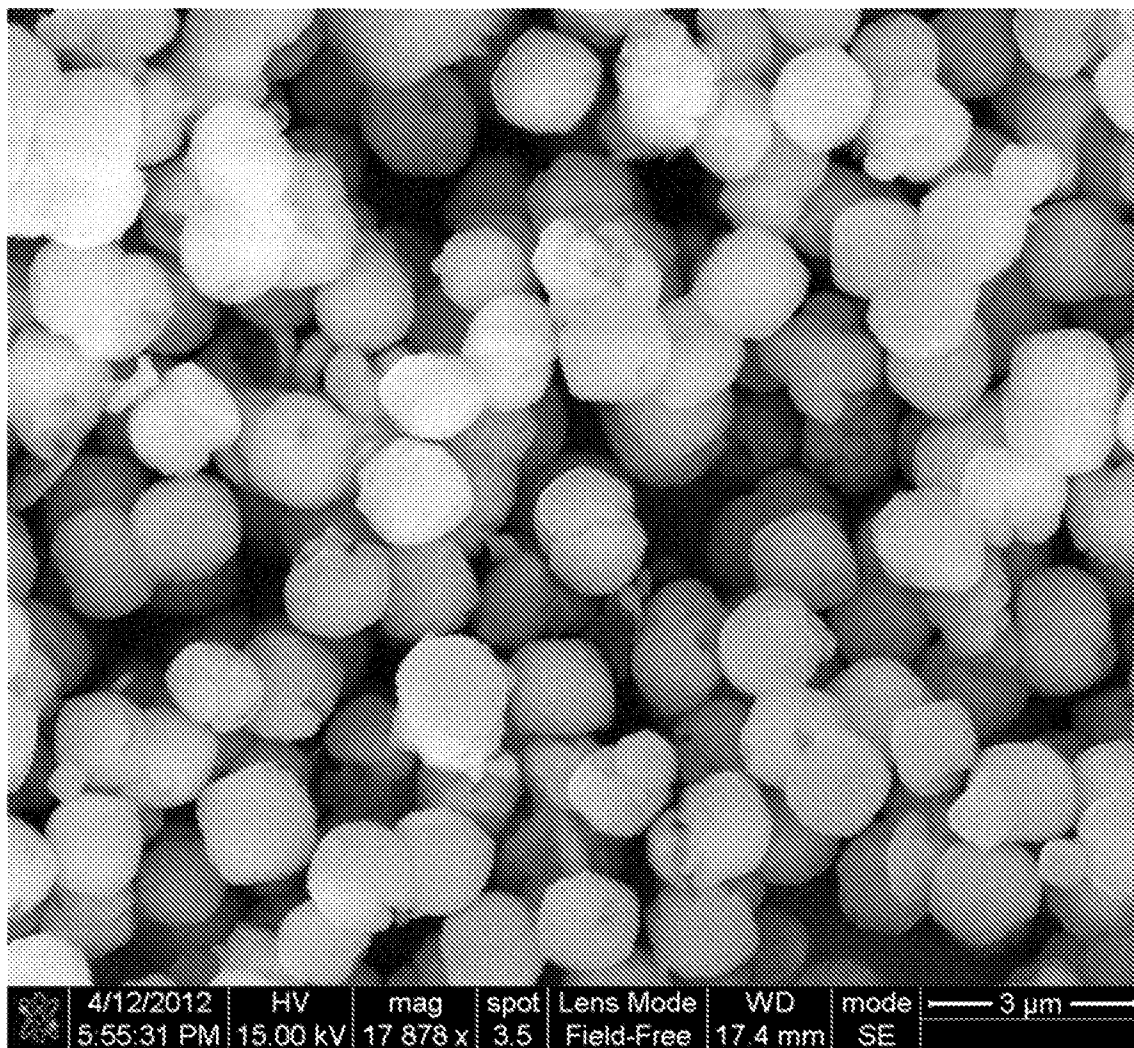


FIG. 1A

**FIG. 1B**

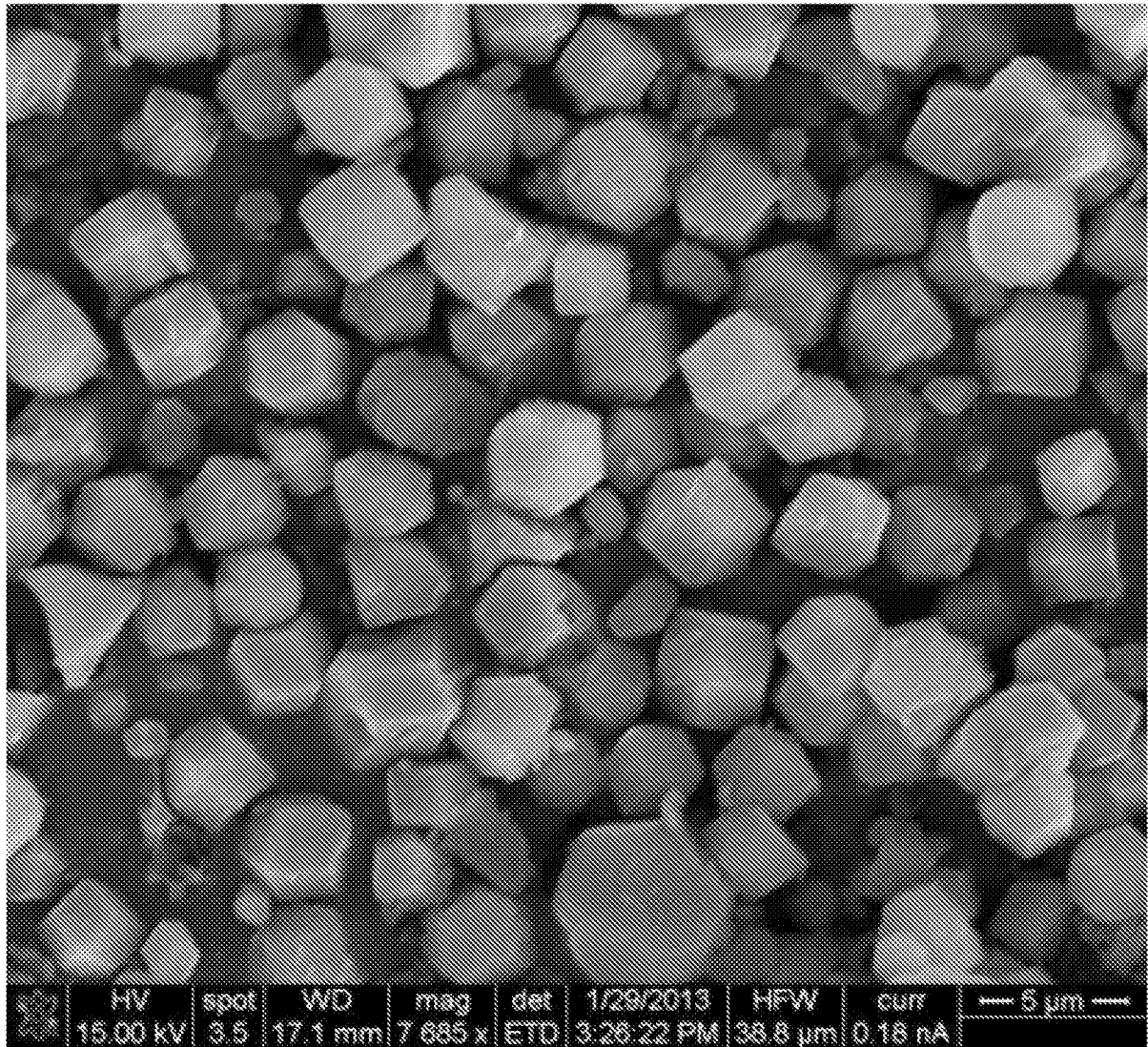


FIG. 1C

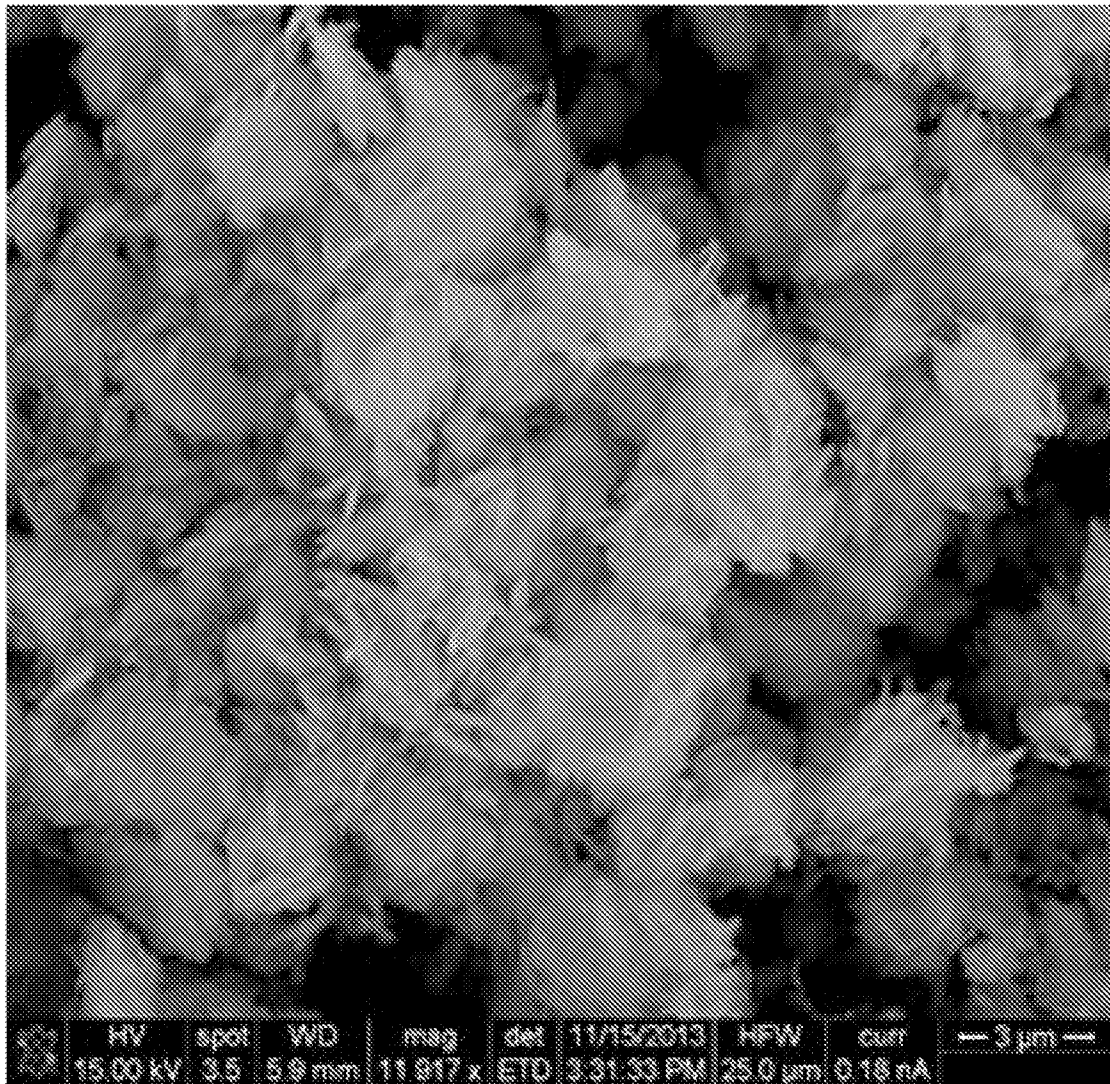
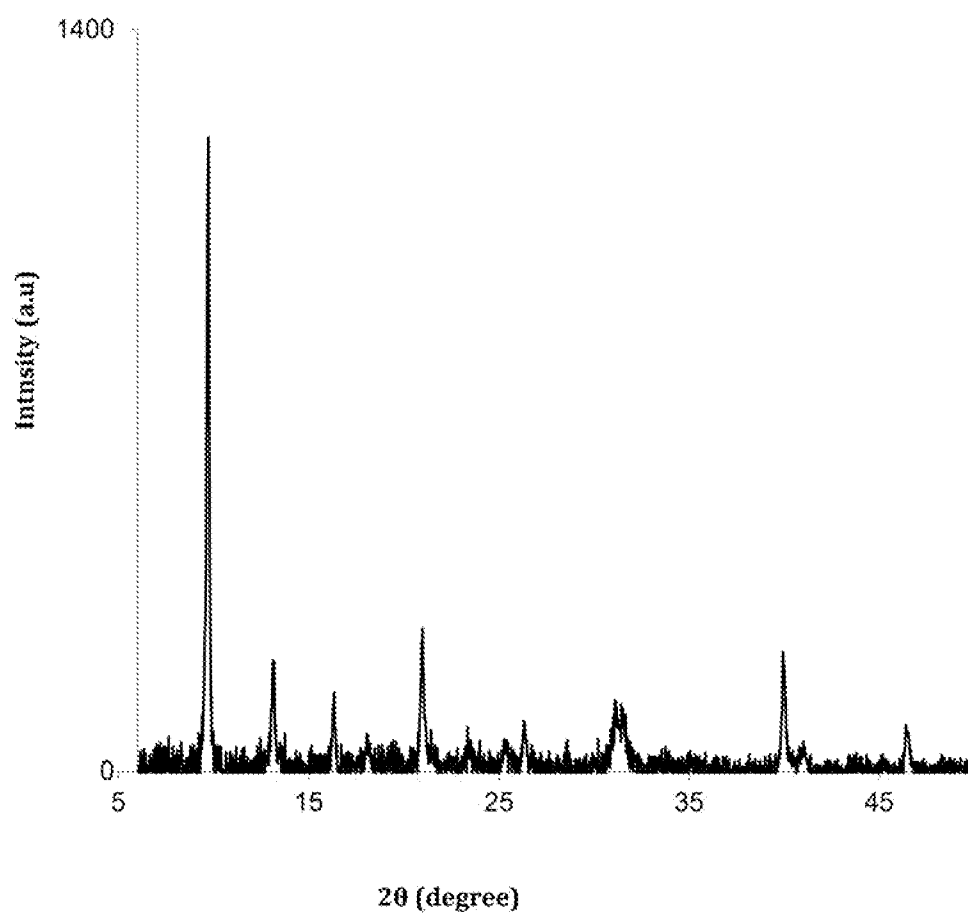
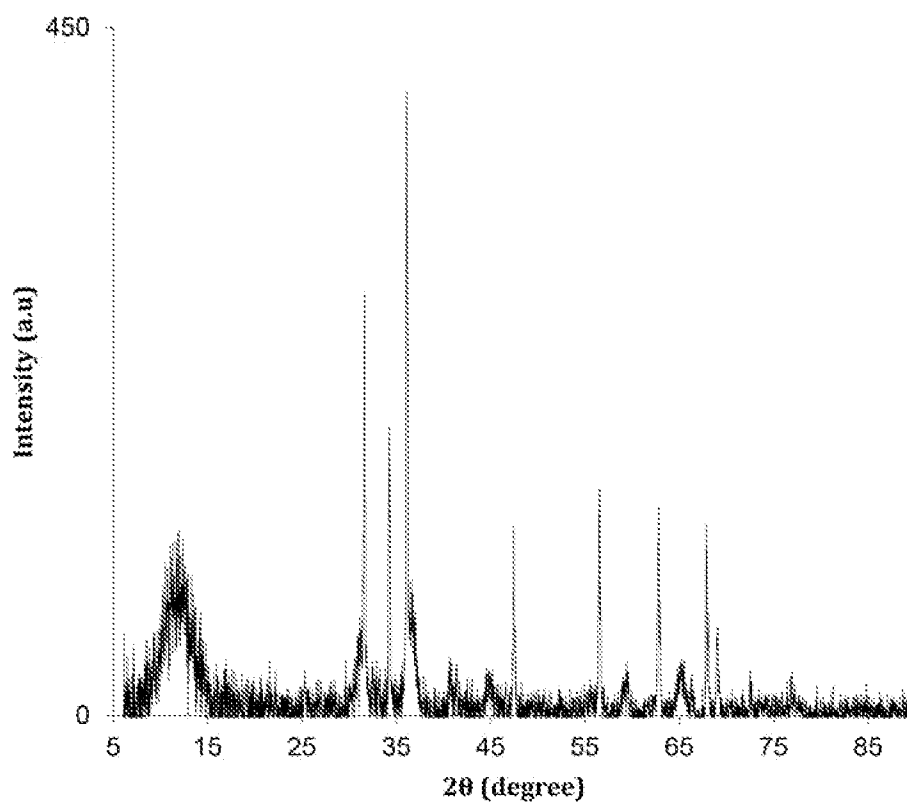


FIG. 1D

**FIG. 2A**

**FIG. 2B**

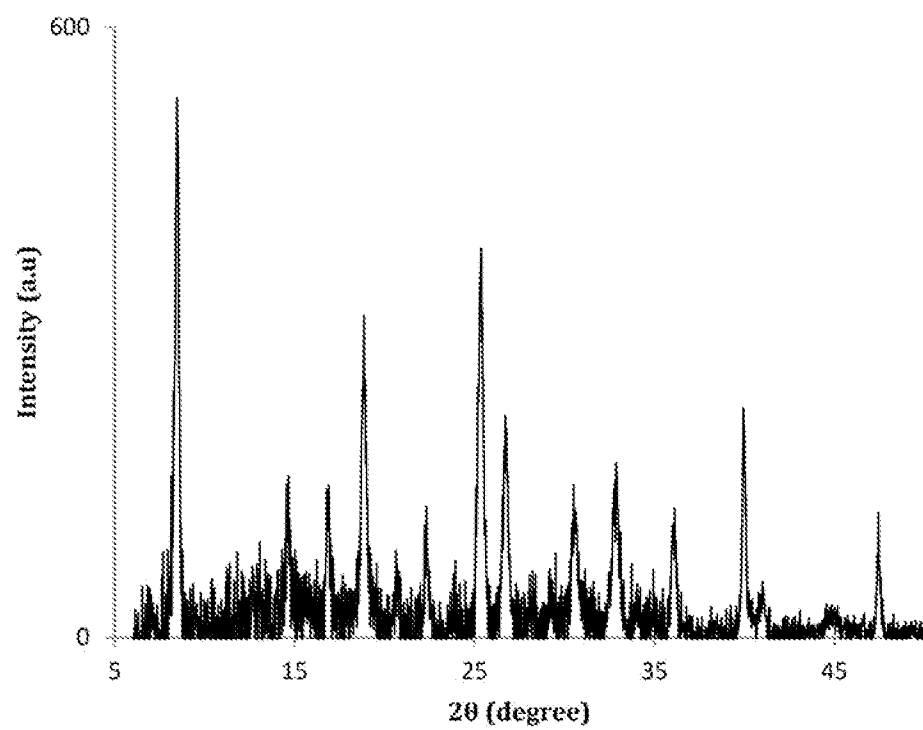
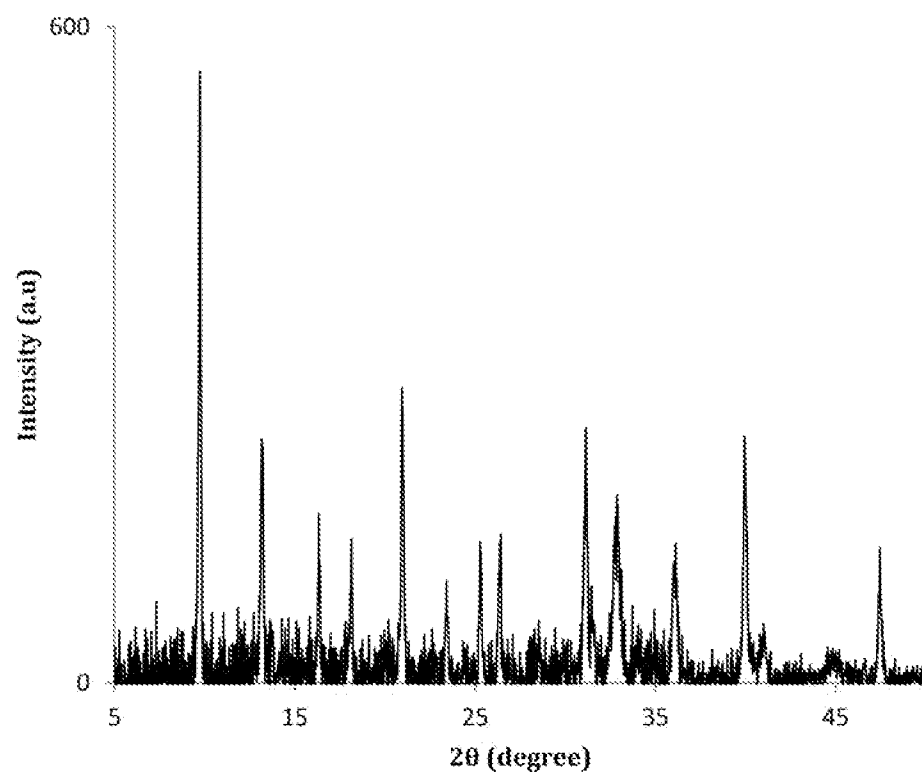


FIG. 2C

**FIG 2D**

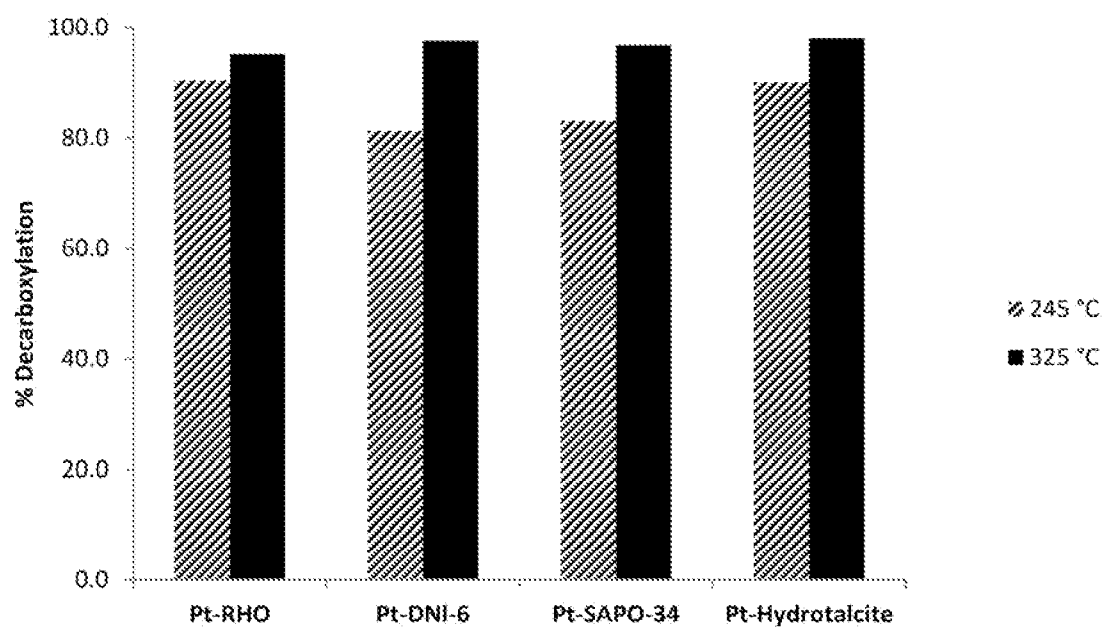


FIG. 3 Decarboxylation of oleic acid over catalysts prepared by salt 1 at different reaction temperature (Reaction conditions: 40 ml oleic acid, 2 g catalyst, 2 hr, and pressure 20 bar at 245 and 325°C)

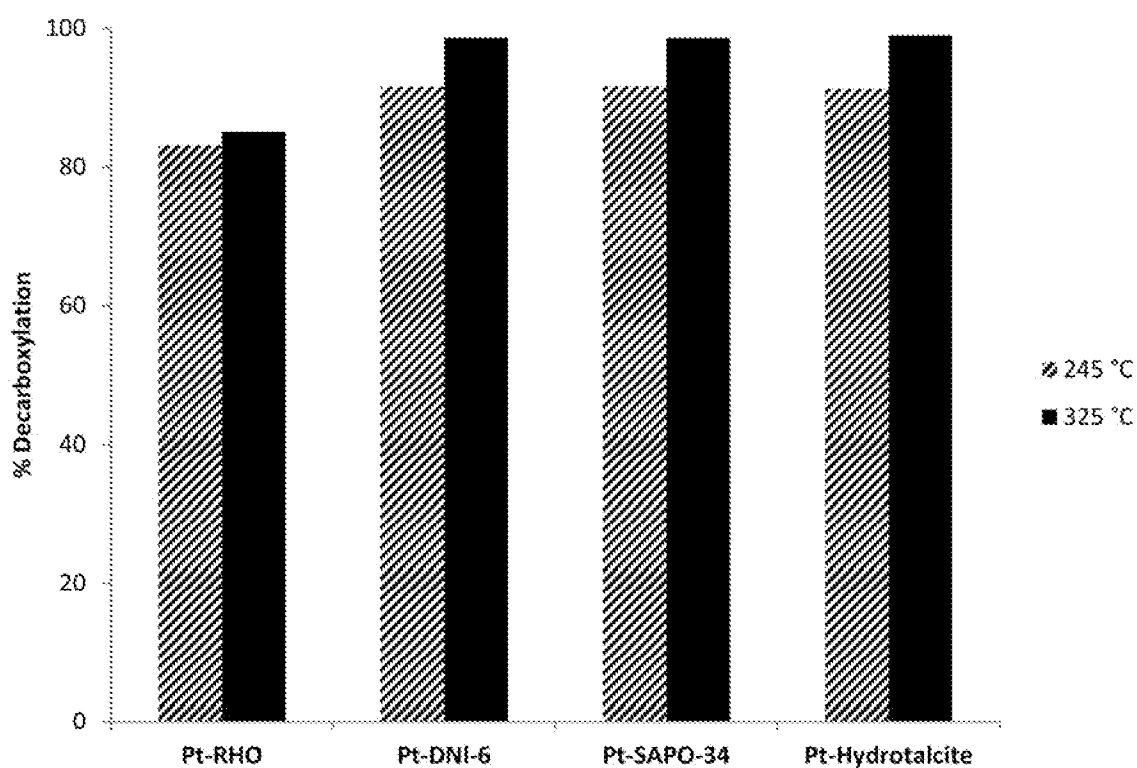


FIG. 4 Decarboxylation of oleic acid over catalysts prepared by salt 2 at different reaction temperature (Reaction conditions: 40 ml oleic acid, 2 g catalyst, 2 hr, and pressure 20 bar at 245 and 325°C)

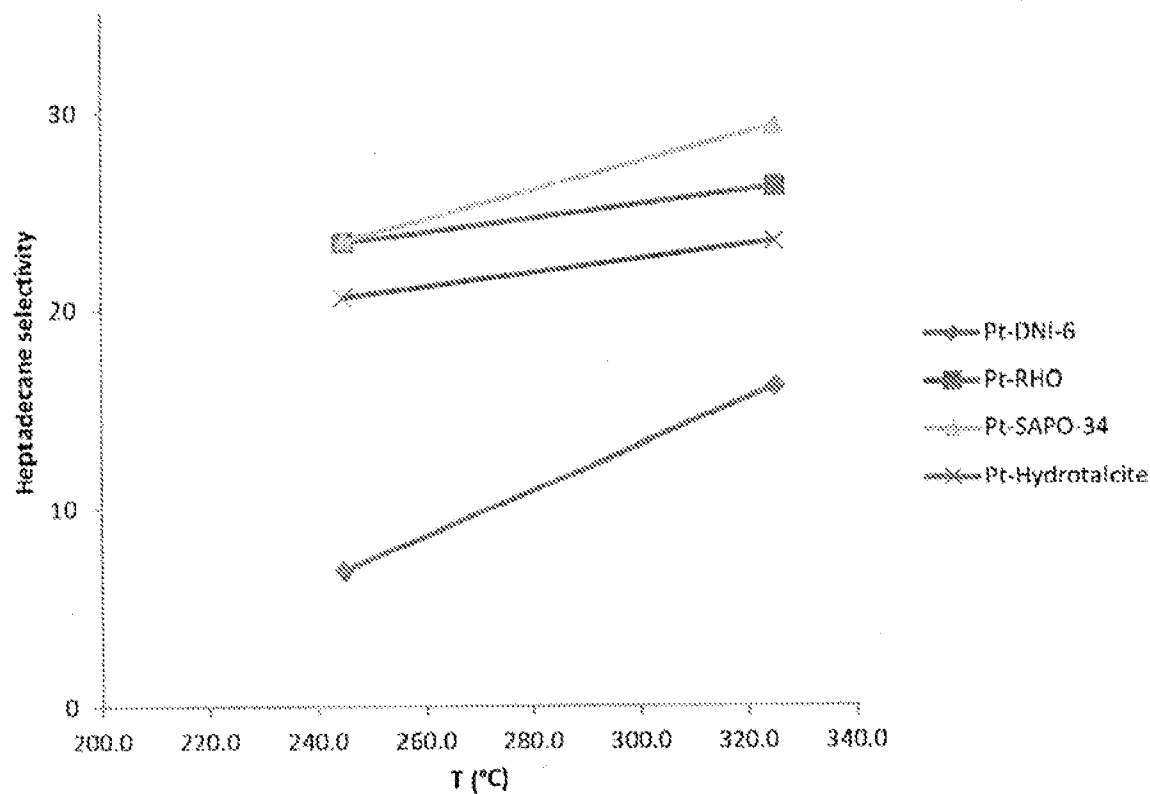


FIG. 5 Effect of temperature and catalyst on heptadecane selectivity in the catalytic deoxygenation of oleic acid (Pt was impregnated on the supports by salt 1)

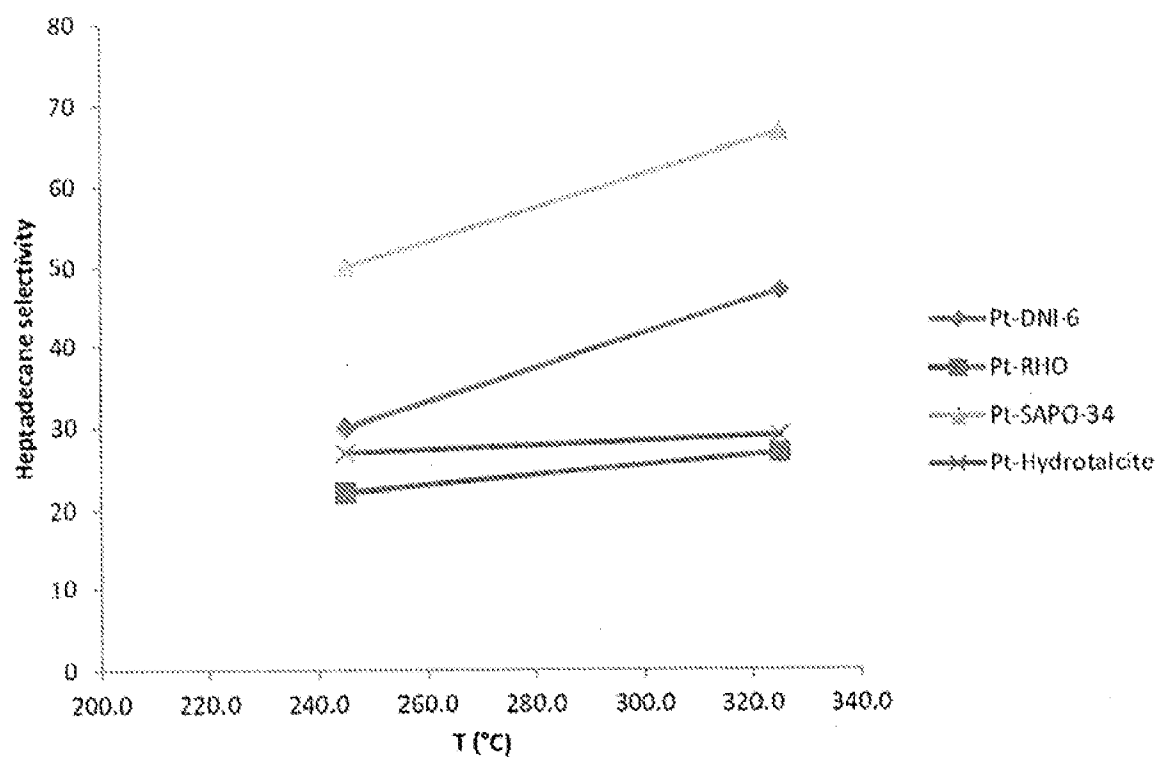


FIG. 6 Effect of temperature and catalyst on heptadecane selectivity in the catalytic deoxygenation of oleic acid (Pt was impregnated on the supports by salt 2)

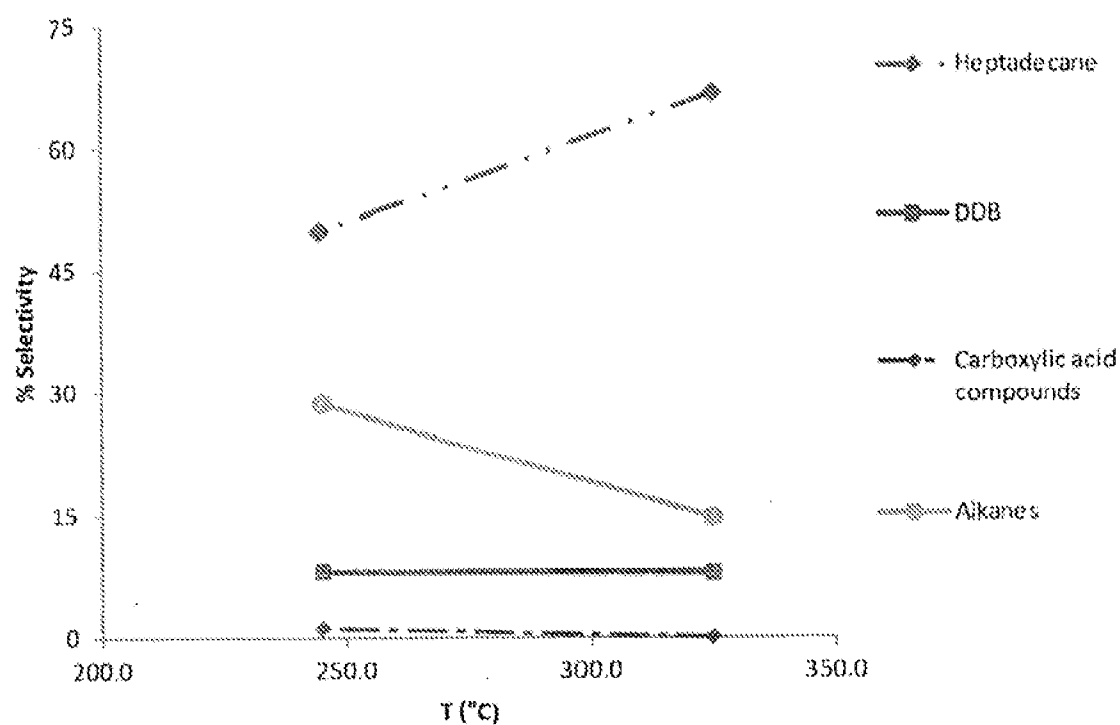


FIG. 7 Effect of temperature on selectivity of the final products in the catalytic deoxygenation of oleic acid over Pt/SAPO-34. (Pt was impregnated on the supports by salt 2)

FIG. 8A

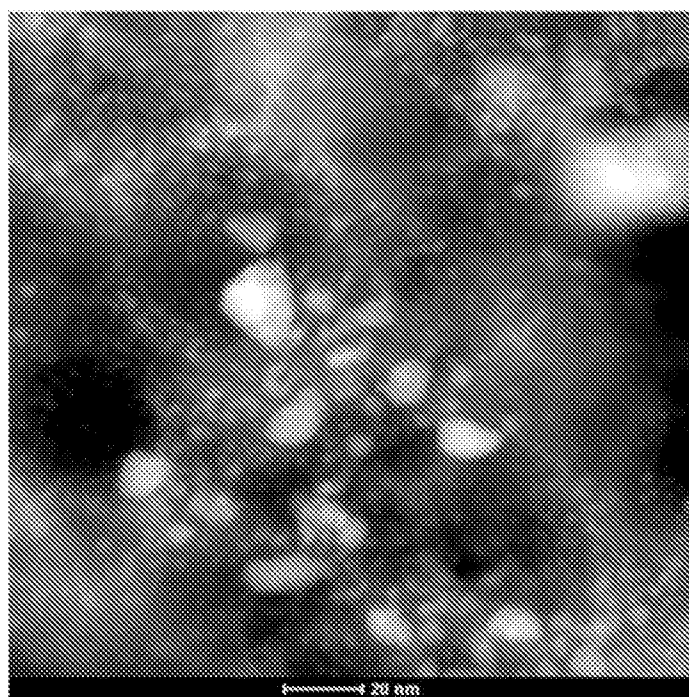
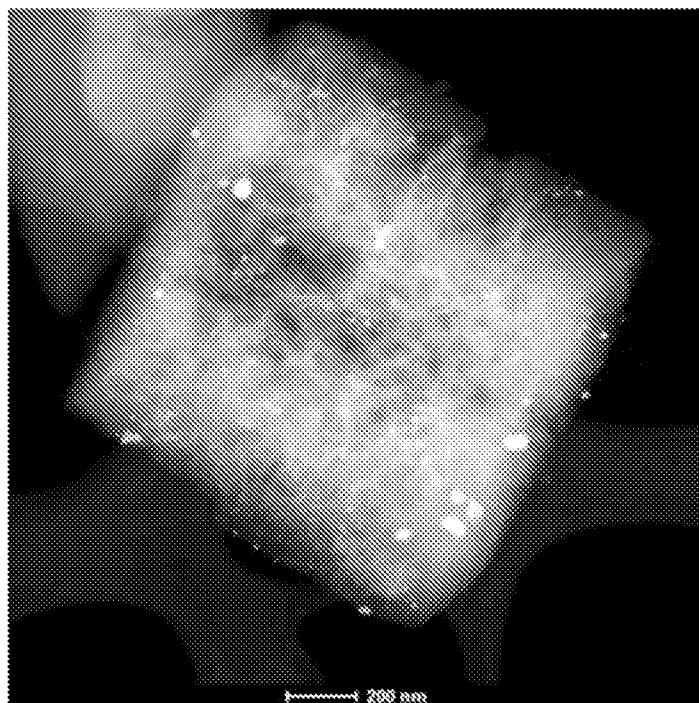


FIG. 8B

FIG. 8C

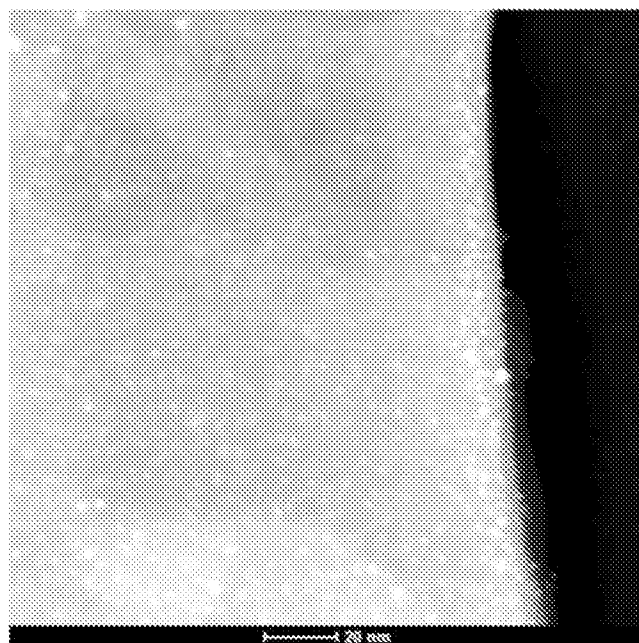
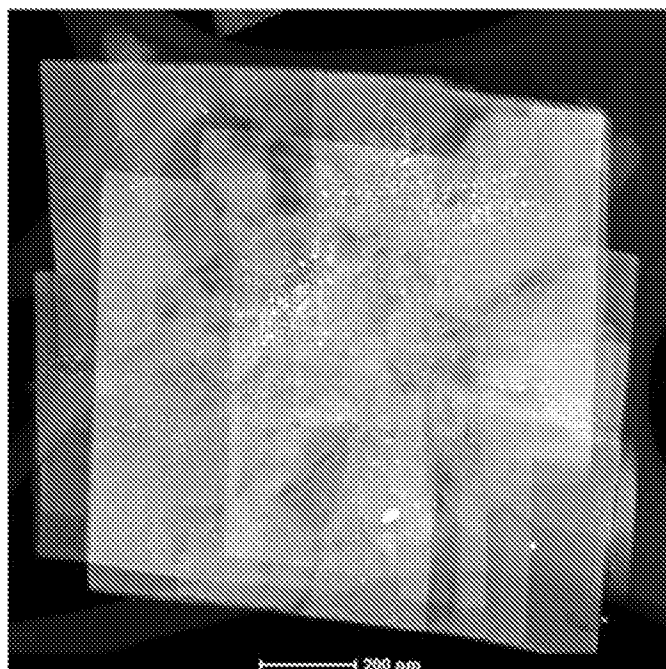
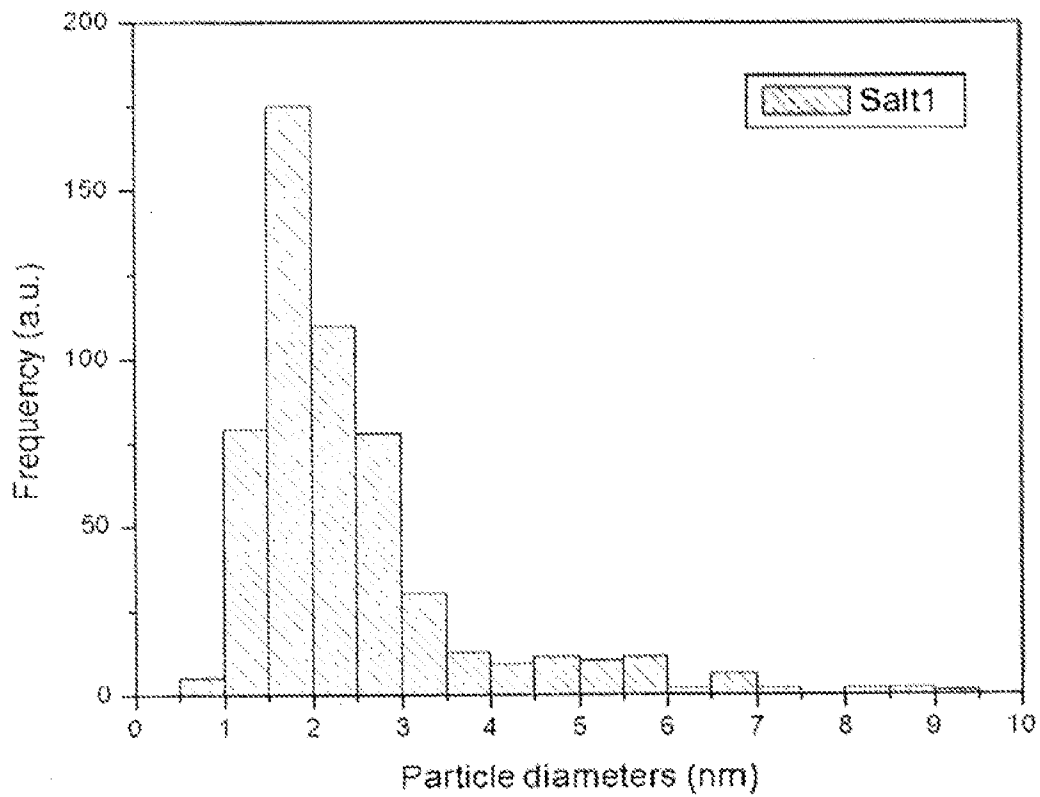


FIG. 8D

**FIG. 9A**

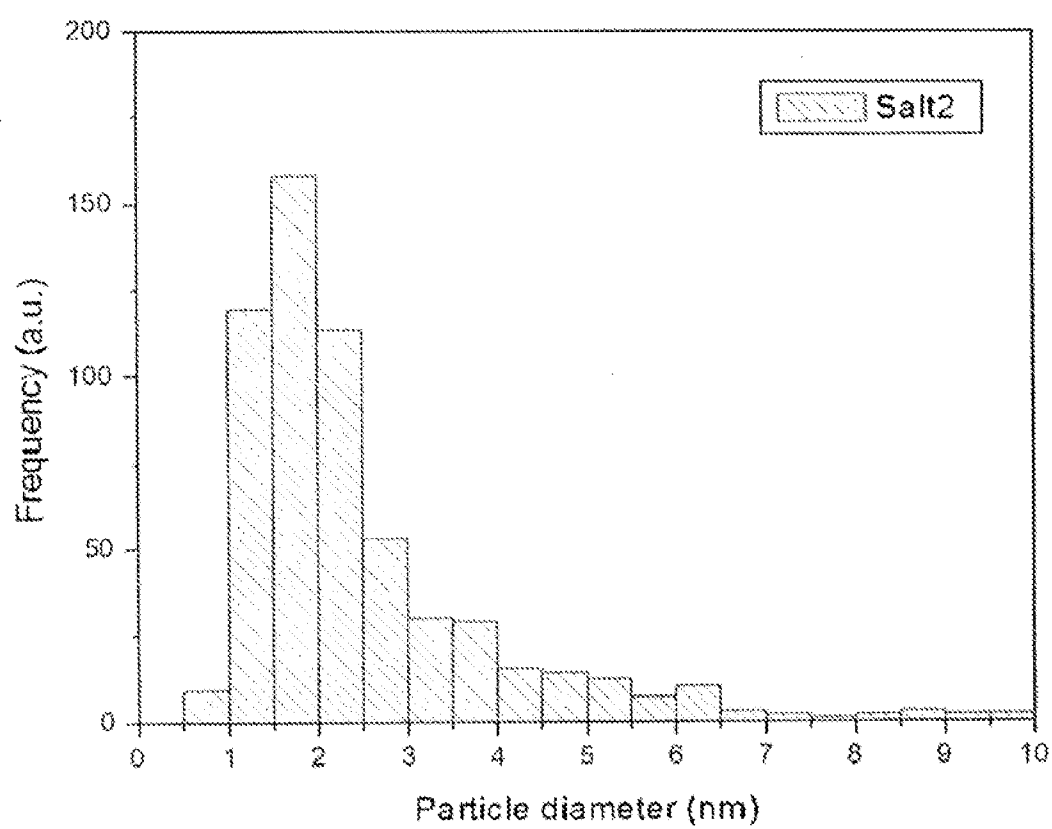
**FIG. 9B**

FIG. 10

Catalyst	Salt ^{1,2}	T (°C)	Product distribution (%wt)																Stearic acid	Oleic acid	Carboxylic compounds	alkene ⁵	%gas
			Hexane	Heptane	Octane	Nonane	Decane	Undecane	Dodecane	Tridecane	Tetradecane	Pentadecane	Hexadecane	Heptadecane	Octadecane	Nanododecane	UDB ³	DBD ⁴					
Pt-DNI-6	Salt 1	325	4.1	4.1	4.7	2.4	5.3	5.9	7.6	5.3	2.9	4.7	5.7	16.2	4.7	5.3	0	5.3	0	0.1	0	4.7	11
Pt-DNI-6	Salt 1	245	5.3	4.1	3.5	6.3	4.1	5.3	5.9	3.5	4.7	4.3	7.1	6.8	4.1	4.1	0	5.3	0	7.6	4.1	2.9	11
Pt-DNI-6	Salt 2	325	4.1	2.9	4.1	4.2	2.9	2.5	3.5	3.3	2.4	2.9	2.4	4.7	2.4	1.8	0.5	2.9	0	0	0	0.2	10
Pt-DNI-6	Salt 2	245	4.8	4	5.5	4	3.4	2.8	3.4	4.5	5.7	4.9	3	3.0	3.6	3.9	0.1	3.3	0	0.4	2.3	0	10.4
Pt-RHO	Salt 1	325	4.7	3.5	5.3	3.5	5.3	4.7	3	4.7	2.9	3.5	4.7	26.3	3.5	3	0	4.4	0	0.2	0.1	4.7	12
Pt-RHO	Salt 1	245	5.3	4.7	4.1	2.9	4.7	4.1	2.4	3.5	4.1	3.5	2.9	23.4	3.5	2.4	0	7	0	0.9	5.3	5.3	10
Pt-RHO	Salt 2	325	4	3.3	4.6	3.9	5	3.2	4.7	4	4.3	4.9	3.7	2.7	3.2	3.2	0	3.6	0	0.3	4	4.1	9
Pt-RHO	Salt 2	245	3.8	2.9	4.1	4.3	4.9	3.7	3.9	4.5	5.6	4.3	3.7	2.2	4.3	3.4	0.1	5.8	0	0.4	4.2	3.7	10.4
Pt-SAPO-34	Salt 1	325	2.4	5.3	3.5	3.9	2.1	3.2	3.5	3.1	3.4	3.1	2.4	29.4	4.7	3.5	0	8.4	0	0.3	3.8	4	10
Pt-SAPO-34	Salt 1	245	2.7	5.1	3.8	2.7	4.7	3.9	3.5	3.9	3.6	4.3	3.4	23.5	4.7	3.6	0.2	8.8	0	0.5	4.2	2.9	10
Pt-SAPO-34	Salt 2	325	0.8	1.2	1.4	1.4	0.8	0.6	1.2	1.1	1.8	1.5	1.8	66.9	1	0.2	0	8	0	0.3	0	1	9
Pt-SAPO-34	Salt 2	245	2.6	1.5	2.3	2.2	3.4	2.2	2.4	2.7	2.1	1.9	3.2	5.0	1.2	0.9	0	8.2	0	0.7	1.1	0.9	10.5
Pt-Hydrolalite	Salt 1	325	4.1	4.7	3.5	4.7	4.1	5.3	4.7	4.1	3.8	4.7	4.1	23.5	5.3	4.7	0.1	2.9	0	0.2	0	4.5	11
Pt-Hydrolalite	Salt 1	245	4.1	4.7	3.8	4.7	5.4	5.3	4.7	4.1	4.5	4.7	4.1	20.6	5.3	4.7	0.1	2.9	0	0.5	0.1	4.7	11
Pt-Hydrolalite	Salt 2	325	2.9	4.1	3.1	3.8	4.7	3.9	4.7	3.5	4.1	3.1	4.7	29.2	4.7	4.1	0	3.1	0	0	0	4.3	12
Pt-Hydrolalite	Salt 2	245	1.8	2.4	3.5	4.1	2.9	2.8	4.1	4.6	4.7	3.5	4.1	2.7	4.7	3.5	0	6.1	0	0.6	3.5	4.1	12

¹ Salt 1: potassium hexachloroplatinate² Salt 2: tetraamminePt nitrate³ Undecylbenzene⁴ Dodecylbenzene⁵ Nonanoic acid, Decanoic acid, Undecanoic acid⁶ Undecene, Dodecene, Tridecene, Tetradecene, Hexadecene, Heptadecene, Octadecene

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 15/18625

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C01B 33/36; B01J 29/04 (2015.01)

CPC - C01B 39/02; C01B 39/026; B01J 20/186

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC(8)-C01B 33/36; B01J 29/04 (2015.01)Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
CPC-C01B 39/02; C01B 39/026; B01J 20/186
USPC-423/700, 60,64Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PatBase, Google Patents, Google Scholar (without Patents)
Keywords: conducting single catalytic reaction production of hydrocarbons fatty acid supported catalyst platinum metal component SAPO-34 SAPO-11 DNL-6 RHO hydrotalcite isolating hydrocarbon reaction products

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ----- Y	US 2012/0203040 A1 (Ratnasamy) 09 August 2012 (09.08.2012) Abstract, para [0010], para [0012], para [0021], para [0013], para [0016], para [0017], para [0031], para [0034], para [0035], para [0063]	1-2,7-13 ----- 3-6,14-16
Y	US 2011/0105817 A1 (Zwijnenburg et al.) 05 May 2011 (05.05.2011) Abstract, para [0007], para [0020], para [0022], para [0029], para [0030], Table 2-5	3-6,14-16
Y	US 2014/0046101 A1 (Ratnasamy et al.) 13 February 2014 (13.02.2014) Abstract, para [0020],	1-16
Y	US 2006/0138025 A1 (Zones et al.) 29 January 2006 (29.01.2006) Abstract, para [0014]-[0017]	1-16
Y	Ahmadi et al.; Decarboxylation and further transformation of oleic acid over bifunctional Pt/SAPO-11 catalyst and Pt/chloride Al ₂ O ₃ catalysts; J. Mol. Catalysis A: Chemical vol 386 pp 14-19; available online 15 February 2014 (15.02.2014) Abstract, pg 15 col 2 para 1; pg 17 Table 1; pg 18 col 1 para 4	1-16

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04 May 2014 (04.05.2014)

Date of mailing of the international search report

10 JUN 2015

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