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Introduction

The rapid depletion of fossil fuels and the tight carbon dioxide emission limits necessitate the production of liquid fuels from new resources. Biomass, which is renewable, CO_2 -neutral and abundant, is a prospective substitute. The long chain (C_{12} - C_{22}) fatty acid compounds in the triglyceride structures make it possible to produce high quality transportation fuels from oils, which cannot be directly used as fuels due to their high viscosity, low volatility and instability.^{1,2} Substantial research has been carried out to convert plant oils into fuels. Fatty acid esters, the first generation of biodiesel, are produced by the transesterification of plant oils with alcohols.^{3–5} However, the poor flow properties of the obtained biodiesel at low temperatures limit its application in engines.^{6–8} Since long-chain hydrocarbons are the major components in diesel, the empha-

Catalytic conversion of Jatropha oil to alkanes under mild conditions with a Ru/La(OH)₃ catalyst \dagger

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The long-chain alkanes obtained from the hydrodeoxygenation of plant oils are ideal substitutes for diesel. In this work, a new efficient catalytic system was established for the conversion of plant oil to long-chain alkanes under mild conditions with a bi-functional Ru/La(OH)₃ catalyst. The hydrodeoxygenation of stearic acid was performed in an autoclave with Ru-based catalysts with different supports (HZSM-5, SiO₂–Al₂O₃, SiO₂, ZrO₂, Mg(OH)₂, La(OH)₃, and La₂O₃). Among these catalysts, Ru supported on basic La(OH)₃ showed a remarkable catalytic performance for the reaction. Over 98% of long-chain alkanes were obtained with 100% conversion of stearic acid at 200 °C and 4 MPa H₂. When crude Jatropha oil was hydrogenated, about 80.7 wt% of long chain alkanes were obtained under the optimized conditions (200 °C, 4 MPa H₂, 8 h). The high efficiency of the Ru/La(OH)₃ catalyst could be due to a coeffect of the high hydrogenation activity of Ru and the basic La(OH)₃ support which can attract the acidic raw material. Additionally, the Ru/La(OH)₃ catalyst was recycled four times and maintained a good activity and stability. The reaction pathway was also explored by using stearic acid as a model compound. Hydrogenation–decarbonylation could be the main pathway to produce *n*-heptadecane, which has one carbon atom less than stearic acid.

sis of recent research focuses on the conversion of oil to diesel-range alkanes, the second generation of biodiesel, instead of esters.

Hydrotreatment has been widely studied and carried out efficiently for the transformation of plant oils. Sulfided Ni-Mo and Co-Mo are conventional hydrotreating catalysts. However, the harsh reaction conditions and sulfur leaching hinder their applications.9-18 Supported Pt, Pd, and Ni catalysts also show high activity and selectivity for the conversion of plant oils to alkanes.16-27 Murata et al. prepared a Pt/HZSM-5 catalyst, which showed a good activity for the hydrotreatment of Jatropha oil and vegetable oils to long-chain alkanes at 270-300 °C. When Pt/HZSM-5 was modified with rhenium, a high oil/cat. ratio (up to 10) was also applicable for the hydrotreatment process with a 67 wt% yield of long-chain alkanes.¹⁹ Lercher's group reported that Ni/ZrO2 and Ni/HBeta were efficient and stable catalysts.^{20,21} In the presence of Ni/ZrO₂, 75 wt% yield of liquid alkanes and 70 wt% yield of n-heptadecane were obtained from hydrotreating microalgae oil at 270 °C through hydrogenolysis/hydrogenation-decarbonylation route. In addition, in the presence of Ni/Hbeta, the dehydration of alcohol intermediates was the main path and led to 60 wt% yield of octadecane from hydrotreating microalgae oil at 260 °C. Recently, carbon supported tungsten- or molybdenumbased materials were also used as catalysts for converting biomass-derived fatty acids to hydrocarbons at 350 °C.²⁸⁻³⁰

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Since it is necessary to consider the energy input during liquid fuel production, the milder the conversion conditions, the higher the energy efficiency. In this study, we use supported Ru catalysts for the hydrotreatment of Jatropha oil, a kind of renewable but inedible plant oil, under mild conditions to produce $C_{15}-C_{18}$ alkanes. The catalysts with different supports (HZSM-5, ZSM-5, SiO₂-Al₂O₃, SiO₂, ZrO₂, Mg (OH)₂, La(OH)₃, and La₂O₃) were prepared and characterized by different techniques. Stearic acid was used as a model compound to investigate the effect of the support, temperature, hydrogenation pressure and solvent. The stability of the optimal catalyst was tested. The reaction pathways for fatty acids and Jatropha oil were also investigated.

Experimental

La(NO₃)₃·6H₂O (99.99% metals basis), stearic acid (\geq 98.0%, AR), stearic alcohol (>99.0%, AR) and *n*-eicosane (>99.0%, AR) were purchased from Aladdin Reagents (Shanghai) Co., LTD. MgCl₂·6H₂O (\geq 98%, AR), ammonium hydroxide (AR) and SiO₂ were purchased from Sinopharm Chemical Reagent Co., Ltd. Crude Jatropha oil was provided by Yunnan Shenyu New Energy Co., Ltd. SiO₂-Al₂O₃ and ZrO₂ were obtained from Saint-Gobain NorPro. ZSM-5 and HZSM-5 were purchased from the catalyst plant of Nankai University. All chemicals were obtained commercially and used without further treatment.

Preparation of the catalysts

La(OH)₃ was prepared by a precipitation method. First, 4.33 g of La(NO₃)₃·6H₂O was dissolved in 200 mL of water and stirred for 2 h. Then 2 M ammonia hydroxide was added into the mixture to adjust the solution pH to 10 and this was then stirred at room temperature for another 2 h. Then the solid was filtered off, washed and dried overnight at 105 °C. After calcination at 700 °C for 4 h, the solid was stirred for 2 h in water. La(OH)₃ was obtained after filtration and dried at 40 °C for 12 h.

The catalysts were prepared by a deposition precipitation method. A calculated amount of the support (HZSM-5, ZSM-5, $SiO_2-Al_2O_3$, SiO_2 , ZrO_2 , $Mg(OH)_2$ or $La(OH)_3$) was first dispersed in water and then a water solution of $RuCl_3 \cdot 3H_2O$ was added and the mixture was stirred at room temperature for 2 h. Subsequently, 2 M ammonia hydroxide was added into the mixture to adjust the solution pH to 10 and this was then stirred at room temperature for another 2 h. After filtration, washing and drying overnight at 40 °C, the catalysts were reduced in a H₂ and N₂ atmosphere at 280 °C for 3 h. The flow rate of hydrogen and nitrogen was 10 and 100 mL min⁻¹, respectively.

As for Ru/La₂O₃, a calculated amount of La_2O_3 was first dispersed in acetone and then added an acetone solution of RuCl₃·3H₂O was added and the mixture was stirred at room temperature for 2 h. After filtration and drying overnight at 40 °C, the catalyst was reduced in a H₂ and N₂ atmosphere at

280 °C for 3 h. The flow rate of hydrogen and nitrogen was 10 and 100 mL min $^{-1}$, respectively.

Characterization of the catalysts

FT-IR spectra were recorded on a Nicolet 8700 FT-IR spectrometer. The samples were prepared as follows: 0.2 g of the support (HZSM-5, ZSM-5, SiO₂-Al₂O₃, SiO₂, ZrO₂, Mg(OH)₂, La(OH)₃, or La₂O₃) was mixed with 20 mL of a 0.05 M *n*-hexane solution of stearic acid and this was stirred at room temperature for 2 h. Then the solid was separated from the mixture by centrifugation. After washing with *n*-hexane 20 times, the residue was dried at 120 °C for 12 h in a N₂ atmosphere.

Nitrogen adsorption measurements were performed using a Coulter SA 3100 adsorption analyzer, which reports the adsorption isotherm, specific surface area and pore volume automatically. The Brunauer–Emmett–Teller (BET) equation was used to calculate the surface area over a range of relative pressures between 0.05 and 0.20. The pore size was calculated from the adsorption branch of the isotherms using the thermodynamic based Barrett–Joyner–Halenda (BJH) method.

A micromeritics ASAP 2020 analyzer (Tristar II 3020M) was used to measure the CO chemisorption isotherms. The dispersion was calculated according to the CO chemisorption results.

XRD analysis was conducted on an X-ray diffractometer (TTR-III, Rigaku Corp., Japan) using Cu K α radiation (λ = 1.54056 Å). The data were recorded over a 2 θ range of 10–70°.

XPS data was obtained with an X-ray photoelectron spectrometer (ESCALAB250, Thermo-VG Scientific, USA) using monochromatized Al K α radiation (1486.92 eV).

The characterization of the $\rm Ru/La(OH)_3$ catalyst is given in the ESI.†

Experimental procedure

In a typical test, 1 mmol of stearic acid (or 0.2 g of Jatropha oil), 0.2 g of Ru/La(OH)₃, and 20 mL of n-hexane were added into a 50 mL Parr reactor with a quartz lining. After purging the reactor with H₂, the reaction was conducted with 4 MPa H₂ (room temperature) at 200 °C for 4 h with a stirring speed of 1000 rpm. The reactor was heated from room temperature to the reaction temperature at a ramp rate of 10 °C min⁻¹. After the reaction, the reactor was put into water straight away to cool it down to room temperature. The liquid, gas and solid were taken out for further analysis. The liquid products were analyzed by a gas chromatograph (GC, Kexiao 1690) with an OV1701 capillary column. Both injection and detection temperatures were 320 °C. The column temperature was kept at 250 °C. n-Eicosane was used as the internal standard to determine the product amount. N2 was used as a carrier gas and the column head pressure was 0.1 MPa. The products were identified by a GC (Agilent 7890A)-mass spectrometer detector (Agilent 5975C with a Triple-Axis Detector) with a HP-5 column. The column temperature was increased from 40 to 180 °C at a ramp rate of 20 °C min⁻¹ and then to 280 °C at a ramp rate of 5 °C min⁻¹. Both the injection and detection

temperatures were 320 °C. Highly pure helium was used as a carrier gas and the flow rate was 1 mL min⁻¹.

The conversion and selectivity were calculated by mol% when stearic acid was used as the starting reactant:

$$Conv.(\%) = \left(1 - \frac{\text{molar amount of stearic acid after reaction}}{\text{molar amount of stearic acid in the starting material}} \times 100\%\right)$$

$$Sel.(\%) = \frac{\text{molar amount of each product}}{\text{molar amount of the converted stearic acid}} \times 100\%$$

The yield was calculated by wt% when Jatropha oil was used as the starting reactant:

$$Yield(wt\%) = \frac{weight of each product}{weight of starting material} \times 100\%$$

The separated catalyst was dried at 40 °C after filtration and sequential washing with acetone. During the catalyst stability test, the catalyst was then reused without any further treatment.

Results and discussion

Analysis of Jatropha oil

The composition of Jatropha oil is shown in Table 1. The main elementary composition of Jatropha oil is C (76.99%), H (11.77%), O (10.58%), and N (0.66%). The predominant fatty acids in Jatropha oil are oleic acid (36.7%), linoleic acid (39.1%), palmitic acid (15.3%) and stearic acid (7.1%).

Catalyst screening

Because Jatropha oil mainly consists of triglycerides and fatty acids, stearic acid was selected as a model compound to test the hydrotreatment process with Ru supported on different carriers (the characterization of the catalysts is shown in Table S1†). As shown in Table 2, the main hydrogenated products obtained from stearic acid (C_{18} carboxylic acid) were

Table 1	Composition of Jatropha oil
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Composition		Content/%
Elementary compositio	on	
C		76.99
Н		11.77
0		10.58
N		0.66
Fatty composition ^a		
Myristic	14:0	1.1
Palmitic	16:0	15.31
Palmitoleic	16:1	0.52
Stearic	18:0	7.1
Oleic	18:1	36.72
Linoleic	18:2	39.05
Arachidic	20:0	0.20

 a The nomenclature shows the number of carbon atoms and the degree of instauration.

			Sel./%					
Entry	Catalyst	Conv./%	<i>n</i> -C ₁₇	<i>n</i> -C ₁₈	C^b	A^b	\mathbf{E}^{b}	
1	Ru/HZSM-5	39.8	5.5	1.4	1.4	50.7	0.7	
2	Ru/ZSM-5	38.5	1	0.8	0.8	53.6	_	
3	Ru/SiO ₂ -Al ₂ O ₃	47.3	29.3	1.6	14.8	41.1	2.9	
4	Ru/SiO ₂	67.2	26.9	1.9	5.5	32.4	0.4	
5	Ru/ZrO_2	82.8	60.6	1.8	2.5	27.5	_	
6	$Ru/Mg(OH)_2$	91.5	78.5	2.3	4.6	1.9	_	
7	$Ru/La(OH)_3$	100	95.9	2.1	0.3	_	_	
8	Ru/La_2O_3	71.5	91	3.1	1.5	1.5	_	
9	$La(OH)_3$	58.4	1.1	—	—	_	_	

^{*a*} Reaction conditions: 1 mmol stearic acid, 0.2 g Ru-catalyst, 4 MPa H₂, 4 h, and stirring at 1000 rpm. ^{*b*} C: cracking products, A:1-octadecanol, E: stearyl stearate.

n-heptadecane, n-octadecane, 1-octadecanol, and cracking products (C9-16 alkanes). The activity of Ru/HZSM-5 and Ru/ZSM-5 were very low under 200 °C (entries 1 and 2). The conversion of stearic acid was 39.8% and 38.5%, respectively, while the selectivity for long-chain alkanes was only 8.3% and 2.6%, respectively, and the major product was 1-octadecanol (50.7% and 53.6% selectivity, respectively). Ru/SiO₂-Al₂O₃ and Ru/SiO₂ showed moderate catalytic activity, and the selectivity for alkanes was 45.7% and 34.3%, respectively (entries 3 and 4). The selectivity for the cracking products was up to 14.8% when using Ru/SiO₂-Al₂O₃ as the catalyst. That is, Ru/SiO₂-Al₂O₃ tends to produce lighter alkanes by C-C cleavage. The conversion of stearic acid was 82.8% with 64.9% of long-chain alkanes over the Ru/ZrO2 catalyst (entry 5). From entries 6 and 7, it can be seen that the Ru catalysts supported on basic hydroxide supports (Mg(OH)₂ and La(OH)₃) showed high activity for converting stearic acid into long chain alkanes. When stearic acid was hydrotreated in the presence of the Ru/ Mg(OH)₂ catalyst at 200 °C and 4 MPa H₂, 78.5% of n-heptadecane, 2.3% of n-octadecane and 4.6% of cracking products were obtained with 91.5% stearic acid conversion. The Ru/La (OH)₃ catalyst exhibited a more outstanding activity: 95.9% of n-heptadecane, 2.1% of n-octadecane and 0.3% of cracking products were obtained with 100% conversion. When La2O3 was employed as the support, the conversion decreased to 71.5% (entry 8). Pure La(OH)₃ was also tested as a catalyst, and showed very low catalytic activity. The conversion of stearic acid was 58.4% and the yield of n-heptadecane was 1.1% (entry 9).

The high efficiency of the Ru/La(OH)₃ catalyst could be due to a co-effect of the metal and support. Ru is an efficient hydrogenation metal. The acidic raw material would be easily adsorbed on the surface of the basic support due to their special acid–base properties, and then be efficiently hydrogenated to alkanes over Ru. To explore the interactions between the supports and substrates, the supports were treated with the stearic acid solution. The treated samples were analyzed by FT-IR to check whether there is adsorbed stearic acid (Fig. 1).

Fig. 1 IR spectra of the supports. The dotted lines represent the untreated supports and the solid lines represent the treated supports.

The peaks at 2961 cm⁻¹ (the C-H stretching vibration of -CH₃), 2920 and 2877 cm⁻¹ (the C-H stretching vibration of -CH₂), 1701 cm⁻¹ (the C=O stretching vibration) and 946 cm⁻¹ (the OH wagging vibration of -COOH) are the characteristic peaks of stearic acid. In the IR spectra of the treated ZrO₂, Mg(OH)₂, La(OH)₃, and La₂O₃ supports, the peaks at 2961, 2920, and 2877 cm^{-1} were much stronger than those of the treated HZSM-5, ZSM-5, SiO₂-Al₂O₃, and SiO₂ supports, which indicates that more organic species were adsorbed on these supports. However, the peaks at 1701 and 946 cm⁻¹ disappeared in the spectra of the treated supports. This indicates that no free stearic acid exists on the supports. Some new peaks were found for the treated ZrO_2 , $Mg(OH)_2$, $La(OH)_3$, and La₂O₃ supports compared with the untreated samples, while new peaks were barely found for the treated HZSM-5, ZSM-5, SiO₂-Al₂O₃, and SiO₂ supports. Stearic acid could exist as a new form on these supports. For the ZrO₂ sample, the new peaks at 1536 and 1467 cm^{-1} could be attributed to the C=O

stretching vibration of carboxylates. In the research performed by Lercher's group, it was proposed that stearic acid was adsorbed at oxygen vacancies in ZrO₂ to form carboxylates.²¹ The new peaks in the spectra of the treated $Mg(OH)_2$, $La(OH)_3$, and La₂O₃ supports are also attributed to the C=O stretching vibration of carboxylates, so stearic acid also existed as carboxylates on the basic supports. The new peaks appeared in the treated $La(OH)_3$ (1540 and 1467 cm⁻¹) and La_2O_3 (1539 and 1468 cm⁻¹) supports were almost at the same positions, while these peaks were different in the treated $Mg(OH)_2$ support $(1567 \text{ and } 1468 \text{ cm}^{-1})$, indicating that the interactions between stearic acid and the support were different for different metal (hydr)oxides. The different interactions may cause the big difference in the selectivity for long-chain alkanes with the La or Mg catalyst. As shown in Table 2, the product distribution with Ru/La(OH)₃ (95.9% n-heptadecane, 2.1% n-octadecane, and 0.3% cracking products) and Ru/La2O3 (91% n-heptadecane, 3.1% n-octadecane, 1.5% 1-octadecanol, and 1.5% cracking products) were similar. However, the product distribution was quite different when Mg(OH)₂ was employed as the support (78.5% n-heptadecane, 2.3% n-octadecane, 1.9% 1-octadecanol, and 4.6% cracking products). Compared with $La(OH)_3$, the structure of La_2O_3 changed greatly after stearic acid treatment. The peaks at about 3607 and 648 cm⁻¹, the characteristic peaks for La(OH)3,31 increased significantly. In other words, La2O3 is unstable and reacts with stearic acid to form La(OH)₃ during the treatment process. Moreover, the carbon content in the La_2O_3 support (2.71%) was lower than in the La(OH)₃ support (6.19%) (see Table S2[†]). Combining this with the fact that the Ru content and dispersion on Ru/La₂O₃ were lower than on Ru/La(OH)₃, this may cause the lower activity of the La2O3 supported catalyst. Based on all the above observations, in the reaction system, the substrate should be adsorbed on the basic support to form carboxylates and then it can be easily catalyzed by Ru to produce alkanes.

Effect of the reaction conditions

The effect of the reaction conditions was investigated. The results are shown in Table 3. At a lower temperature (180 °C), only 50.2% of stearic acid was converted and the major product was 1-octadecanol (40.1% selectivity). While at a higher temperature (220 °C), the selectivity of *n*-heptadecane decreased to 91.6% and more cracking products (4.2% selectivity) were obtained. A temperature around 200 °C was suitable for the conversion of stearic acid to long-chain alkanes, and the conversion could be fulfilled in 4 hours. The hydrotreating pressure also influenced the stearic acid conversion. At a lower pressure (2 MPa H₂), the conversion was 70.6%, and the selectivity of *n*-heptadecane was 82.7%. While at a higher pressure (6 MPa H₂), more *n*-octadecane (3.8%) and cracking products (5.0%) were obtained. Both a higher temperature and higher pressure tend to produce cracking products.

The effect of solvents was also investigated. When nonane or dodecane was used as the solvent, the product distribution was similar to when hexane was used as the solvent (Table 3, entries 1, 6 and 7). Stearic acid can also be hydrogenated in



Table 3 Stearic acid conversion over the Ru/La(OH)₃ catalyst^a

Entry	Solvent	T/°C	H ₂ /MPa	Conv./%	Sel./%				
					<i>n</i> -C ₁₇	<i>n</i> -C ₁₈	C^b	A^b	E^b
1	Hexane	200	4	100	95.9	2.1	0.3	_	_
2	Hexane	180	4	50.2	25.9	1.4	0.4	40.1	0.1
3	Hexane	220	4	100	91.6	2.8	4.2	_	_
4	Hexane	200	2	70.6	82.7	1.7	1.3	4.4	0.1
5	Hexane	200	6	100	92.6	3.8	5.0	_	_
6	Nonane	200	4	100	96.6	1.7	0.6	_	_
7	Dodecane	200	4	100	97.9	1.9	0.2	_	_
8	H_2O	200	4	93.4	83.6	4.9	1.2	0.8	0.9

^{*a*} Reaction conditions: 1 mmol stearic acid, 0.2 g Ru/La(OH)₃, 4 MPa H₂, 4 h, and stirring at 1000 rpm. ^{*b*} C = cracking products, A = 1-octadecanol, E = stearyl stearate.

aqueous solution, although it is insoluble in water (Table 3, entry 8). The conversion (93.4%) was lower than that in alkane solvents, and the *n*-heptadecane selectivity decreased to 83.6% and the *n*-octadecane selectivity increased to 4.9%. In aqueous solution, the conversion and selectivity of *n*-heptadecane both decreased.

Conversion of Jatropha oil

Crude Jatropha oil was hydrotreated in the presence of the Ru/ La(OH)₃ catalyst at 200 °C and 4 MPa H₂. The time-course of the product distribution for the transformation of Jatropha oil is shown in Fig. 2. Fatty acids (hexadecanoic acid and stearic acid) and the corresponding alcohols (1-hexadecanol and 1-octadecanol) were detected in the first 4 h. The yield of fatty acids and fatty alcohols first increased and then decreased to 0. The yield of long-chain alkanes, mainly *n*-heptadecane and *n*-pentadecane, increased with time. After 8 h, 80.7 wt% alkanes were obtained and odd carbon number chain alkanes were the main products (64.8 wt% yield of *n*-heptadecane and 11.7 wt% yield of *n*-pentadecane). The collected gas contained 5.2 wt% yield of CH₄, 2.7 wt% yield of C₃H₈ and trace C₂H₆. Based on the carbon content, 89.1% of carbon in Jatropha oil



$$R \xrightarrow{\downarrow} OH \longrightarrow RH + CO_2$$
(2)

$$R \xrightarrow{\downarrow} OH + 3H_2 \longrightarrow RCH_3 + 2H_2O$$
(3)



was converted to liquid alkanes. The total carbon balance was 97%. It can be seen that the $Ru/La(OH)_3$ catalyst is effective for converting Jatropha oil to alkanes under mild conditions (Scheme 1).

Moreover, the recyclability of the Ru/La(OH)₃ catalyst was examined. A batch of Ru/La(OH)₃ was repeatedly used for the conversion of Jatropha oil. As shown in Fig. 3, the catalyst maintained a good activity after being used four times. Although the yield of long-chain alkanes decreased, it was still around 70 wt% in the 4th run. The yields of *n*-hexadecane and *n*-octadecane slightly increased in runs 2–4.

The fresh and used catalysts were characterized. There was no significant difference in the XRD patterns of the Ru/La



Fig. 2 Product distribution for the transformation of Jatropha oil over $Ru/La(OH)_3$ at 200 °C as a function of time. Reaction conditions: 0.2 g Jatropha oil, 0.2 g $Ru/La(OH)_3$, 200 °C, and stirring at 1000 rpm.



Fig. 3 The performance of the catalyst in the recyclability experiments.

Table 4 Characteristics of the $Ru/La(OH)_3$ catalyst before and after being used four times

	BET surface area $(m^2 g^{-1})$	Pore volume $(cm^3 g^{-1})$	Pore size (nm)	Ru/wt%	C/%
Fresh	15.2	0.077	19.1	1.56	0.65
Used	6.0	0.040	26.7	1.43	4.69

 $(OH)_3$ catalyst (Fig. S4[†]). As shown in Table 4, after using the catalyst four times, the surface area and pore volume of the Ru/La(OH)₃ catalyst decreased, while the pore size increased. The content of Ru decreased from 1.56% to 1.43%. The carbon content in the catalyst increased from 0.65% to 4.69%. According to all of the characterization data, the activity decrease of the catalyst could be mainly due to the pore structure change, Ru leaching and the active site coking.

Mechanism of the reaction

The deoxygenation of fatty acids can occur in three ways: decarbonylation [Scheme 1, eqn (1)], decarboxylation [Scheme 1, eqn (2)], and hydrodeoxygenation [Scheme 1, eqn (3)].^{32,33}

Taking stearic acid as an example, as the major products were alkanes with one carbon atom less (n-heptadecane), decarbonylation [eqn (1)]/decarboxylation [eqn (2)] could be the main reaction pathways when catalyzed by Ru/La(OH)₃. Very few stearic acid molecules were converted through hydrodeoxygenation [eqn (3)] since it was difficult for the basic catalyst to convert alcohols to alkanes through dehydration and hydrogenation. Because hydrogen is not necessary for the decarboxylation step, one reaction was conducted in a N2 atmosphere. However, only 0.11% n-heptadecane, coming from the decarboxylation of stearic acid, was detected after the reaction. Trace CO_2 was also detected in the gas phase, therefore the decarboxylation step existed but was not the main deoxygenation process under these conditions. Moreover, from the data in Table 3, the hydrogen pressure influenced the reaction. Therefore, stearic acid was converted mainly through the decarbonylation process, indicating that Ru/La(OH)₃ was more conducive to catalyze the decarbonylation reaction rather than hydrodeoxygenation or decarboxylation reactions. There was no CO but CH₄, trace CO₂ and trace C₂H₆ in the gas phase collected after the reaction. The CH₄ could come from the methanation of CO.17-19,34 Another potential source of organic gas (CH₄ and C₂H₄) could be from the C-C cleavage of alkanes over the Ru-catalyst.

To further explain the decarbonylation process, the conversion of stearic acid was explored with $Ru/La(OH)_3$ (Fig. 4). Trace *n*-octadecane and cracking products (<0.9%) were detected. The yield of *n*-heptadecane continuously increased over 4 h to 95.9% with increasing conversion, while the yield of 1-octadecanol increased gradually to 36.4% and then decreased at higher conversion. It can be inferred that 1-octadecanol was an intermediate product.



Fig. 4 The conversion of stearic acid. Reaction conditions: 1 mmol n-octadecanol, 0.2 g Ru/La(OH)₃, 200 °C, 4 MPa H₂, and stirring at 1000 rpm.

Octadecanal was not detected during the conversion because it was unstable and converted to either *n*-heptadecane or 1-octadecanol. 1-Octadecanol was tested in a separate experiment on Ru/La(OH)₃ under the same conditions to explore the conversion process (Fig. 5). The yield of *n*-heptadecane increased almost linearly with 1-octadecanol conversion, but only trace *n*-octadecane (<0.7%) was formed *via* the hydrodeoxygenation reaction. 1-Octadecanol mainly underwent the dehydrogen–decarbonylation process,²¹ dehydrogenating to octadecanal, and then decarbonylating to *n*-heptadecane.

According to the discussion on the deoxygenation process of stearic acid, the possible pathway for Jatropha oil conversion is shown in Scheme 2. The first step is the hydrogenation of unsaturated carbon bonds, and then the obtained saturated triglycerides were hydrogenolyzed to propane and saturated fatty acids. This step can be derived from the following observations. From GC-MS analysis on the products obtained after 2 h, a few saturated fatty acid isopropyl/propyl esters and stearic acid were detected, which could come from the hydrogenolysis of triglycerides. No unsaturated fatty acids or esters were detected. Then the saturated fatty acids were mainly hydrogenated to the corresponding aldehyde (RCHO).



Fig. 5 The conversion of *n*-octadecanol. Reaction conditions: 1 mmol *n*-octadecanol, 0.2 g Ru/La(OH)₃, 200 °C, 4 MPa H₂, and stirring at 1000 rpm.

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Scheme 2 The reaction pathway for the hydrotreatment of Jatropha oil.

However, the aldehyde was not detected because it was easily converted to more stable compounds – the linear alkane with one carbon atom less (RH) *via* a decarbonylation process and the corresponding fatty alcohol (RCH₂OH) *via* a hydrogenation process. Most fatty alcohol molecules were converted to the linear alkane (RH) *via* a dehydrogenation–decarbonylation process, and very few of them were converted to the linear alkane with the same carbon number (RCH₃) *via* hydrodeoxy-genation. Meanwhile, the decarboxylation process also existed but can almost be ignored.

Conclusion

In summary, a new efficient catalytic system was established for the hydrodeoxygenation of Jatropha oil to long-chain alkanes under mild conditions with a bi-functional Ru/La (OH)₃ catalyst. At 200 °C and 4 MPa H₂, a relatively high yield (80.7 wt%) of long chain alkanes was achieved. After using four times, about 70 wt% of alkanes was still obtained under the same conditions. It was verified that hydrogenation–decarbonylation could be the main pathway to produce long-chain alkanes from fatty acids. The La(OH)₃ support could adsorb the carboxyl group of the fatty acid, and thus promote the hydrotreatment over the supported Ru catalyst.

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