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PAPER

Catalytic conversion of Jatropha oil to alkanes under mild conditions with Ru/La(OH)$_3$ catalyst

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The long-chain alkanes obtained from hydrodeoxygenation of plant oils are ideal substitutes to 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 bi-functional Ru/La(OH)$_3$ catalyst. The hydrodeoxygenation of stearic acid was performed in an autoclave with Ru-based catalysts with different supports, including HZSM-5, ZSM-5, SiO_2-Al_2O_3, SiO_2, ZrO_2, $Mg(OH)_2$, $La(OH)_3$, and La_2O_3. Among which, Ru supported on basic La(OH)$_3$ showed a remarkable catalytic performance in the reaction. Over 98% of long-chain alkanes were obtained with 100% conversion of stearic acid at 200 °C and 4 MPa H_2. When crude Jatropha oil was hydrogenated, about 80.7 wt% of long chain alkanes were obtained at the optimized conditions (200 °C, 4 MPa H_2, 8 h). The high efficiency of the Ru/La(OH)$_3$ catalyst could be due to the co-effect of high hydrogenation activity of Ru and the basic La(OH)$_3$ support which can attract the acidic raw material. Additionally, the Ru/La(OH)$_3$ was recycled for four times and maintained a good activity and stability. The reaction pathway was also explored by using stearic acid as model compound. Hydrogenation-decarbonylation could be the main pathway to produce *n*-heptadecane, which has one carbon atom less than stearic acid.

Introduction

The rapid depletion of fossil fuels and the tight limitation of carbon dioxide emission necessitate the production of liquid fuels from new resource. Biomass, renewable, CO_2-neutral, and abundant, is a prospective substitute. The long chain (C_{12}-C_{22}) fatty acid compounds in the triglycerides structure make it possible to produce high quality transportation fuels from oil, which cannot be directly used as fuels for the high viscosity, low volatility and instability[1,2]. Substantial researches have been carried out to convert plant oil into fuels. Fatty acid esters, the first generation biodiesel, are produced by the transesterification of plant oils with alcohols[3-5]. However, the poor flow property at low temperature of the obtained biodiesel limits its application in engine[6-8]. Since long-chain hydrocarbons are the major components in diesel, the emphasis of the recent researches focuses on the conversion of oil to diesel-range alkanes, the second generation biodiesel, instead of esters.

Hydrotreatment has been widely studied and carried out efficiently in the transformation of plant oil. 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 showed high activity and selectivity for the conversion of plant oil to alkanes[16-27]. Murata *et al.* prepared Pt/HZSM-5 catalyst which had a good activity for the hydrotreating of Jatropha oil and vegetable oils to long-chain alkanes at 270-300 °C. When modified Pt/HZSM-5 with Rhenium, a high oil/cat. ratio (up to 10) was also applicable for the hydrotreating process with a 67 wt% yield of long-chain alkanes[19]. Lercher's group reported that Ni/ZrO_2 and Ni/HBeta were efficient and stable catalysts[20-21]. In the presence of Ni/ZrO_2, 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 octodecane from hydrotreating microalgae oil at 260 °C. Recently, carbon supported tungsten- or molybdenum-based materials were also used as catalysts for converting biomass-derived fatty acids to hydrocarbons at 350 °C[29,30].

Since it is necessary to consider the energy input during liquid fuel production, the milder the conversion conditions, the higher the energy efficiency can be obtained. In this study, we use supported Ru catalysts for the hydrotreating 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 including HZSM-5, ZSM-5, SiO_2-Al_2O_3, SiO_2, ZrO_2, $Mg(OH)_2$,

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$La(OH)_3$, and La_2O_3 were prepared and characterized by different techniques. Stearic acid was used as model compound to investigate the effect of supports, temperature, hydrogenation pressure, and solvent. The stability of the optimal catalyst was tested. The reaction pathways of fatty acids and Jatropha oil were also investigated.

Experimental

$La(NO_3)_3·6H_2O$ (99.99% metals basis), stearic acid (≥98.0%, AR), stearic alcohol >99.0%, AR) and *n*-eicosane (>99.0%, AR) were purchased from Aladdin Reagents (Shanghai) Co., LTD. $MgCl_2·6H_2O$ (≥98%, AR), ammonium hydroxide (AR) and SiO_2 were purchased from Sinopharm Chemical Reagent Co., Ltd. Crude Jatropha oil was provided by Yunnan Shenyu New Energy Co., Ltd.. SiO_2-Al_2O_3 and ZrO_2 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.

Catalyst Preparation

$La(OH)_3$ was prepared by precipitation method. First, 4.33 g of $La(NO_3)_3·6H_2O$ was dissolved in 200 mL of water and stirred for 2 h. Then 2 M ammonia hydroxide was added into the mixture to adjust solution pH to 10 and stirred at room temperature for another 2 h. Then the solid was filtrated, washed and dried over night at 105 ºC. After calcined at 700 ºC for 4 h, the solid was stirred for 2 h in water. $La(OH)_3$ was obtained after filtrated and dried at 40 ºC for 12 h.

The catalysts were prepared by deposition precipitation method. A calculated amount of 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 added the water solution of $RuCl_3·3H_2O$ and stirred at room temperature for 2 h. Subsequently, 2 M ammonia hydroxide was added into the mixture to adjust solution pH to 10 and stirred at room temperature for another 2 h. After filtration, washing and drying over night at 40 ºC, the catalysts were reduced in a H_2 and N_2 atmosphere at 280 ºC for 3 h. The flow rate of hydrogen and nitrogen was 10 and 100 mL/min, respectively.

As for Ru/La_2O_3, a calculated amount of La_2O_3 was first dispersed in acetone and then added the acetone solution of $RuCl_3·3H_2O$ and stirred at room temperature for 2 h. After filtration and drying over night at 40 ºC, the catalyst was reduced in a H_2 and N_2 atmosphere at 280 ºC for 3 h. The flow rate of hydrogen and nitrogen was 10 and 100 mL/min, respectively.

Characterization of Catalysts

FT-IR spectra were recorded on a Nicolet 8700 FT-IR spectrometer. The samples were prepared as follows: 0.2 g support, including HZSM-5, ZSM-5, SiO_2-Al_2O_3, SiO_2, ZrO_2, $Mg(OH)_2$, $La(OH)_3$, and La_2O_3, respectively, was mixed with 20 mL 0.05 M *n*-hexane solution of stearic acid and stirred at room temperature for 2 h. Then the solid was separated from the mixture by centrifuging. After washed with *n*-hexane for 20 times, the residue was dried at 120 °C for 12 h in N_2 atmosphere.

Nitrogen adsorption measurements were performed using a Coulter SA 3100 adsorption analyzer which reports adsorption isotherm, specific surface area and pore volume automatically. The Brunauer-Emmett-Teller (BET) equation was used to calculate the surface area in the 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 Kα radiation (λ= 1.54056 Å). The data were recorded over 2θ ranges of 10-70°.

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

The characterization of Ru/$La(OH)_3$ catalyst was given in the Supporting Information.

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 H_2, the reaction was conducted with 4 MPa H_2 (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 ºC/min. After reaction, the reactor was put into water at once to cool 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. N_2 was served as 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 Triple-Axis Detector) with an HP-5 column. The column temperature was increased from 40 to 180 °C at a ramp rate of 20 ºC/min and then to 280 °C at a ramp rate of 5 ºC/min. Both injection and detection temperatures were 320 °C. High pure helium was served as carrier gas and the flow rate is 1 mL/min.

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

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

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

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

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

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

Table 1 Characteristics of the Jatropha oil.

Composition		Content/%
Elementary composition		
C		76.99
H		11.77
O		10.58
N		0.66
Fatty composition [a]		
Myristic	14:0	1.1
Palmitic	16:0	15.31
Palmitoliec	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

Table 2 Comparison of stearic acid conversion over different catalysts at 200 °C. [a]

Entry	Catalyst	Conv. /%	Sel./%				
			n-C_{17}	*n*-C_{18}	C^b	A^b	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_2O_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 H_2, 4h, and stirring at 1000 rpm. [b]C: cracking products, A:1-octadecanol, E: stearyl stearate.

Results and Discussion

Analysis of Jatropha oil.

The composition of Jatropha oil was 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 the 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 triglyceride and fatty acids, stearic acid was selected as model compound to test the hydrotreating process with Ru supported on different carriers (the characterization of catalysts were shown in Table S1). As shown in Table 2, the main hydrogenated products obtained from stearic acid (C_{18} carboxylic acid) were *n*-heptadecane, *n*-octadecane, 1-octadecanol, and cracking products ($C_{9\text{-}16}$ alkanes). The activity of Ru/HZSM-5 and Ru/ZSM-5 were very low under 200 °C (entries 1-2). The conversion of stearic acid was 39.8% and 38.5%, respectively, while the selectivity of 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/SiO_2-Al_2O_3 and Ru/SiO_2 showed moderate catalytic activity, and the selectivity of alkanes was 45.7% and 34.3%, respectively (entries 3-4). Specially, the selectivity of cracking products was up to 14.8% when using Ru/SiO_2-Al_2O_3 as catalyst. That is, Ru/SiO_2-Al_2O_3 tend to produce lighter alkanes by C-C cleavage. The conversion of stearic acid was 82.8% with 64.9% of long-chain alkanes over Ru/ZrO_2 catalyst (entry 5). From entries 6-7, it can be seen that the Ru catalysts supported on basic hydroxide support ($Mg(OH)_2$ and $La(OH)_3$) showed high activity on converting stearic acid into long chain alkanes. When stearic acid was hydrotreated in the presence of Ru/$Mg(OH)_2$ catalyst at 200 °C and 4 MPa H_2, 78.5 % of *n*-heptadecane, 2.3% of *n*-octadecane and 4.6% cracking products were obtained with 91.5% of stearic acid conversion. Ru/$La(OH)_3$ catalyst exhibited more outstanding activity. 95.9% of *n*-heptadecane, 2.1% of *n*-octadecane and 0.3% cracking products were obtained with 100% conversion. While, when La_2O_3 was employed as support, the conversion decreased to 71.5% (Table 2, entry 9). Pure $La(OH)_3$ was also tested as catalyst, and showed very low catalytic activity. The conversion of stearic acid was 58.4% and the yield of *n*-heptadecane was 1.1% (Table 2, entry 9).

The high efficiency of the Ru/$La(OH)_3$ catalyst could be due to the co-effect of metal and support. Ru is an efficient hydrogenation metal. The acidic raw material would be easily absorbed on the surface of the basic support for their special acid-base properties, and then be efficiently hydrogenated to alkanes over Ru. To explore the interactions between supports and substrates, the supports were treated by the stearic acid solution. The treated samples were analyzed by FT-IR to check if there is adsorbed stearic acid (Fig. 1).

The peaks at 2961 cm^{-1} (the C-H stretching vibration of -CH_3), 2920 and 2877 cm^{-1} (the C-H stretching vibration of -CH_2), 1701 cm^{-1} (the C=O stretching vibration) and 946 cm^{-1} (the OH wagging vibration of -COOH) were the characteristic peaks of stearic acid. In the IR spectra of treated ZrO_2, $Mg(OH)_2$, $La(OH)_3$, and La_2O_3, the peaks at 2961, 2920, and 2877 cm^{-1} were much stronger than that of treated HZSM-5, ZSM-5, SiO_2-Al_2O_3, and SiO_2, which indicated that more organic species were adsorbed on these supports. However, the peaks at 1701 and 946 cm^{-1} disappeared in the spectra of treated supports. It indicates that no free stearic acid exists on the supports. Some new peaks were found on the treated ZrO_2, $Mg(OH)_2$, $La(OH)_3$, and La_2O_3 compared with the untreated samples, while new peaks were barely found on the treated HZSM-5, ZSM-5, SiO_2-Al_2O_3, and SiO_2. The stearic acid could exist as new form on these supports. For ZrO_2 sample, the new peaks at 1536 and 1467 cm^{-1} could be attributed to the C=O stretching vibration of carboxylates. In the researches performed by Lercher's group, it was proposed that the stearic acid was adsorbed at oxygen vacancies of ZrO_2 to form carboxylates[21]. The new peaks in the spectra of treated $Mg(OH)_2$, $La(OH)_3$, and La_2O_3, were also attributed to the C=O stretching vibration of carboxylates, so the stearic acid also existed as carboxylates on the basic support. The new peaks appeared in the treated $La(OH)_3$ (1540 and 1467 cm^{-1}) and La_2O_3 (1539 and 1468 cm^{-1}) were almost at the same position, while these were different in the treated $Mg(OH)_2$ (1567 and 1468 cm^{-1}), indicating the interaction between stearic acid and support was different in different metal (hydr)oxides. The different interaction may cause the big difference in the selectivity of long-chain alkanes with 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/La_2O_3 (91% *n*-heptadecane, 3.1% *n*-octadecane, 1.5% 1-octadecanol, and 1.5% cracking products) were similar. While, the product distribution

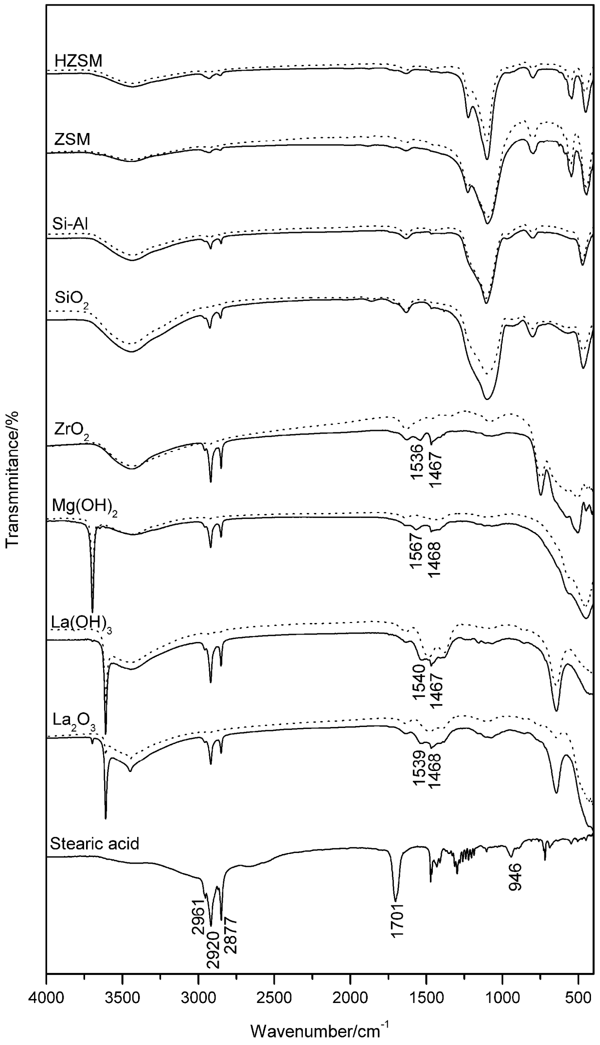


Fig. 1 IR spectrums of the supports. The dot lines represent the untreated supports, and the solid lines represent the treated supports.

(78.5% *n*-heptadecane, 2.3% *n*-octadecane, 1.9% 1-octadecanol, and 4.9% cracking products) was quite different when $Mg(OH)_2$ was employed as support. Compared with $La(OH)_3$ and La_2O_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 of $La(OH)_3$[31], increased significantly, that is, La_2O_3 was unstable and would react with stearic acid to form $La(OH)_3$ during the treatment. Moreover, the carbon content on the La_2O_3 (2.71%) was lower than that of $La(OH)_3$ (6.19%) (see Table S2). Combining the fact that Ru content and dispersion on Ru/La_2O_3 were also lower than that of $Ru/La(OH)_3$, it may cause the lower activity of La_2O_3 supported catalyst. Based on all above observations, in the reaction system, the substrate should be adsorbed on the basic support to form carboxylates and easily catalyzed by Ru to produce alkanes.

Effect of reaction conditions

The effect of reaction conditions was investigated. The results are shown in Table 3. At lower temperature (180 °C), only 50.2% of stearic acid was converted and the major product was 1-octadecanol (40.1% selectivity). While at higher temperature (220 °C), the selectivity of *n*-heptadecane decreased to 91.6% and more cracking products (4.2% selectivity) were obtained. Temperature at 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 lower pressure (2 MPa H_2), the conversion was 70.6%, and the selectivity of *n*-heptadecane was 82.7%. While at higher pressure (6 MPa H_2), more *n*-octadecane (3.8%) and cracking products (5.0%) were obtained. Both higher temperature and pressure tend to produce cracking products.

Table 3 Stearic acid conversion over $Ru/La(OH)_3$ catalysts. [a]

Entry	Solvent	T /°C	H_2 /MPa	Conv. /%	Sel./%				
					n-C_{17}	*n*-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 H_2, 4h, and stirring at 1000 rpm. [b]C= cracking products, A=1-octadecanol, E=stearyl stearate.

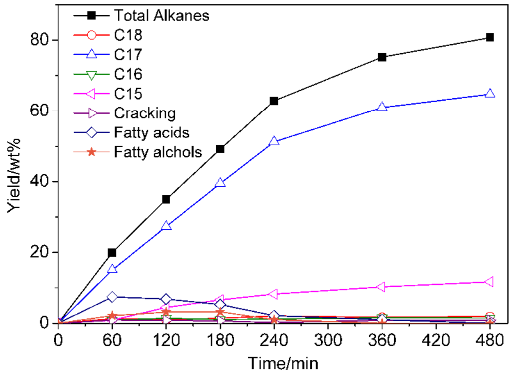


Fig. 2 Product distribution for the transformation of Jatropha oil over $Ru/La(OH)_3$ at 200 °C as a function of time. Reaction conditions: 0.2 g Jatropha oil, 0.2 g $Ru/La(OH)_3$, 200 °C, and stirring at 1000 rpm.

The effect of solvents was also investigated. When nonane or dodecane was used as solvent, the product distribution was similar to which using hexane as solvent (Table 3, entries 1, 6, and 7). The stearic acid can also be hydrogenated in aqueous solution though it was insoluble in water (Table 3, entry 8). The conversion (85.4%) was lower than that in alkane solvents, and the *n*-heptadecane selectivity decreased to 90.6% and the *n*-octadecane selectivity increased to 5.4%. 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

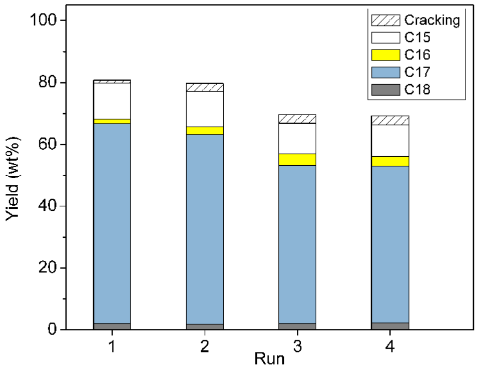


Fig. 3 The performance of the catalyst in the recycle experiment.

Table 4 Characteristics of the Ru/La(OH)$_3$ catalysts before and after used for 4 times.

	BET (m^2/g)	Pore Volume (cm^3/g)	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

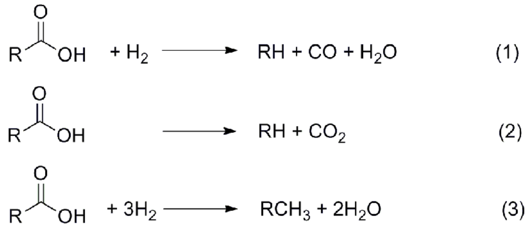
Ru/La(OH)$_3$ catalyst at 200 °C and 4 MPa H_2. The time-course of product distribution for the transformation of Jatropha oil is shown in Fig. 2. The fatty acids (hexadecanoic acid and stearic acid) and corresponding alcohols (1-hexadecanol and 1-octadecanol) were detected in the first 4 h. The yield of fatty acids and fatty alcohols were first increased and then decreased to 0. The yield of long-chain alkanes, mainly *n*-heptadecane and *n*-pentadecane, increased with time extending. 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 CH_4, 2.7 wt% yield of C_3H_8 and trace C_2H_6. Based on the carbon content, 89.1% of carbon in Jatropha oil was converted to liquid alkanes. The total carbon balance was 97%. It can be seen that Ru/La(OH)$_3$ catalyst is effective on converting Jatropha oil to alkanes under mild conditions.

Moreover, the recyclability of Ru/La(OH)$_3$ catalyst was examined. A batch of Ru/La(OH)$_3$ was repeatedly used on the conversion of Jatropha oil. As shown in Fig. 3, the catalyst maintained a good activity after being used for 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*-octodecane slightly increased in runs 2-4.

The fresh and used catalysts were characterized. There was no significant difference in the XRD patterns of Ru/La(OH)$_3$ catalysts (Fig. S4). As shown in Table 4, after used for four times, the surface area and pore volume of 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 on the catalyst increased from 0.65% to 4.69%. According to all of the characterization, 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 acid can occur in three ways, decarbonylation [Equation (1)], decarboxylation [Equation (2)], and hydrodeoxygenation [Equation (3)][32,33].



Scheme 1 Pathway of deoxygenation of fatty acid.

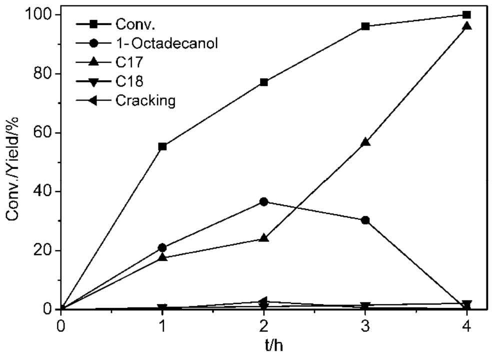


Fig. 4 The conversion of stearic acid. Reaction conditions: 1 mmol *n*-octadecanol, 0.2 g Ru/La(OH)$_3$, 200 °C, 4 MPa H_2, and stirring at 1000 rpm.

Taking the stearic acid as an example, as the major products were alkanes with one carbon atom less (*n*-heptadecane), decarbonylation [Equation (1)]/ decarboxylation [Equation (2)] could be the main reaction pathway when catalyzed by Ru/La(OH)$_3$. Few stearic acid was converted through hydrodeoxygenation [Equation (3)], since it was difficult for the basic catalyst to convert alcohol to alkanes through dehydration and hydrogenation. Because hydrogen was not necessary for the decarboxylation step, one reaction was conducted in N_2 atmosphere. While, only 0.11% *n*-heptadecane, coming from the decarboxylation of stearic acid, was detected after reaction. Trace CO_2 was also detected in the gas phase, therefore, the decarboxylation step exited but was not the main deoxygenation process at this condition. Moreover, from the data in Table 3, the hydrogen pressure influenced the reaction. Therefore, the stearic acid could be converted mainly through decarbonylation process, indicating Ru/La(OH)$_3$ was more conductive to catalyze the decarbonylation rather than hydrodeoxygenation or decarboxylation. While, there was no CO but CH_4, trace CO_2 and trace C_2H_6 in gas phase collected after reaction. The CH_4 could come from the methanation of CO[17-19,34]. Another potential source of organic gas (CH_4 and C_2H_4) could be due to the C-C cleavage of alkanes over 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 to 95.9% for 4 h with increasing conversion, while that 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.

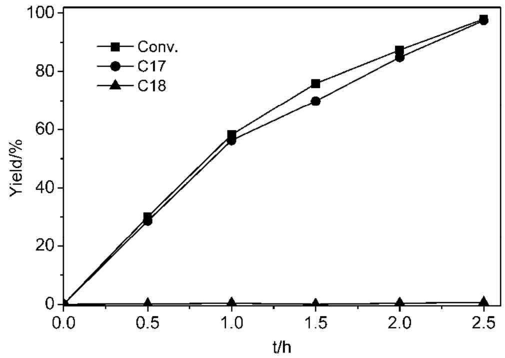


Fig. 5 The conversion of *n*-octadecanol. Reaction conditions: 1 mmol *n*-octadecanol, 0.2 g Ru/La$(OH)_3$, 200 °C, 4 MPa H_2, and stirring at 1000 rpm.

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$(OH)_3$ at 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. 1-Octadecanol mainly underwent the dehydrogen-decarbonylation process [21], dehydrogenating to octadecanal, and then decarbonylating to *n*-heptadecane.

According to the discussion on deoxygenation process of stearic acid, the possible pathway of Jatropha oil conversion was shown in Scheme 2. The first step was 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 products obtained at 2 h, a few saturated fatty acid isopropyl/propyl esters and stearic acid were detected, which could come from the hydrogenolysis of triglyceride. No unsaturated fatty acids or esters were detected. Then the saturated fatty acid was mainly hydrogenated to the corresponding aldehyde (RCHO). While, the aldehyde was not detected for it was easily converted to more stable compounds, the linear alkane with one carbon atom less (RH) via decarbonylation process and the corresponding fatty alcohol (RCH_2OH) via hydrogenation process. Most fatty alcohol was converted to linear alkane (RH) via dehydrogenation-decarbonylation process, and very few of them were converted to linear alkane with same carbon number (RCH_3) via hydrodeoxygenation. Meanwhile, the decarboxylation process also existed but almost can 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 bi-functional Ru/La$(OH)_3$ catalyst. At 200 °C and 4 MPa H_2, a relatively high yield (80.7 wt%) of long chain alkanes was achieved. After used for 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 acid. The La$(OH)_3$ could absorb the carboxyl group of fatty acid, and thus promote the hydrotreating over supported Ru.

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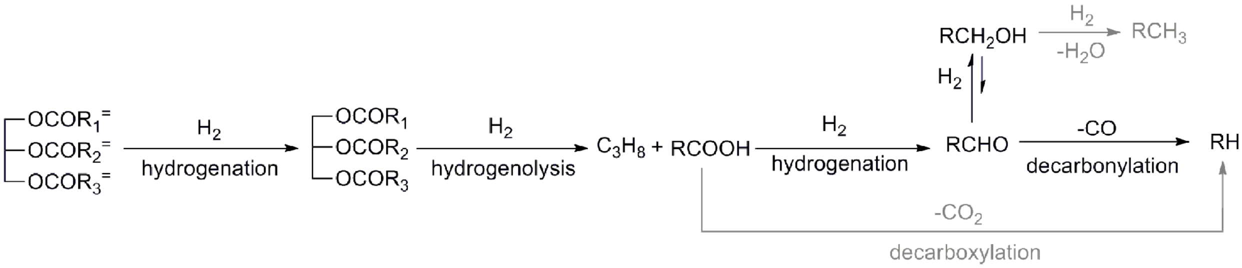

Scheme 2 The reaction pathway of hydrotreating of Jatropha oil.

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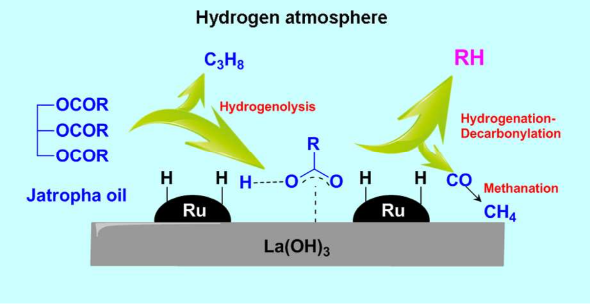

Ruthenium supported on $La(OH)_3$ display good performance on the hydrodeoxygenation of fatty acid and Jotropha oil at 200 °C.