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Catalytic Cracking of Soybean Oil for Biofuel over γ-Al₂O₃/CaO Composite Catalyst

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In this paper, we report the catalytic cracking of soybean oil for biofuel over γ-Al₂O₃/CaO composite catalysts. The influence of catalysts, cracking temperature and weight hourly space velocity (WHSV) on the products distribution were investigated. The maximum yield (70.0 wt.%) of biofuel with low acid value (6.7 mg KOH g⁻¹) and oxygen content (5.6%), as well as high calorific value (44.2 MJ kg⁻¹) was achieved over 35 wt.% γ-Al₂O₃/CaO at 480 °C and 3.72 h⁻¹. The paper focused on the variation of biofuel composition and cracking pathway caused by γ-Al₂O₃/CaO composite catalysts via gas chromatography-mass spectrometry (GC-MS) and thermogravimetric (TG) analysis. Calcium oxide would react with fatty acid to yield calcium carboxylates at 300-350 °C, which were subsequently decomposed into hydrocarbons (57.9 wt.%) and ketones (22.6 wt.%) at 415-510 °C. As for 35 wt.% γ-Al₂O₃/CaO, the addition of γ-Al₂O₃ was beneficial to generate alkenes (38.2 wt.%), arenes (10.6 wt.%) and alcohols (12.3 wt.%) with ketones decreasing (16.5 wt.%) via γ-hydrogen transfer reaction and disproportination.

Keywords: soybean oil, catalytic cracking, γ-Al₂O₃/CaO catalysts, biofuel

Introduction

Severe energy security and environmental pollution have been caused due to extensive use of fossil fuels. Thus, there is a considerable interest in developing renewable and environmentally friendly energy throughout the world.[1] As an important renewable energy source, lipid is a potential feedstock for preparing environmental friendly and carbon neutral biofuel since it possesses a similar structure to the diesel fuel.[1,2] The methods for producing biofuel from lipid mainly include transesterification and cracking.[3-6] It is well known that biodiesel is composed of fatty acid methyl esters (FAME) produced by transesterification of triglycerides and alcohols. The preparation technology is quite mature, but there are still some drawbacks such as poor cold flow properties and relatively low calorific value.[7,8] In this regard, hydrocracking and catalytic cracking have been attempted to convert lipid into biofuel.[8,9] The second-generation biodiesel containing C₁₅₋₁₈ linear paraffins with high quality and yield is achieved by hydrodeoxygenation, decarboxylation and

hydroisomerization of triglycerides, whereas the high cost of hydrogen and the rigorous demand for catalyst activity restrict its industrialization.[10] Among all the preparation technologies of biofuel, catalytic cracking is regarded as a promising method for its simple process and similar liquid product to petroleum-based fuels.[11,12] In addition, catalytic cracking can be applied to produce gasoline, kerosene and diesel with suitable catalysts, and presents good compatibility with various feedstock, as well as relatively lower cost.[13,14] Currently, for purpose of reaching the demand of vehicle fuel standards, catalytic cracking still need to reduce the acid value and oxygen content of the biofuel for improving fuel properties including density, calorific value, dynamic viscosity, etc. There is no doubt that the catalysts play a vital role in the catalytic cracking of lipid for biofuel.

Varieties of catalysts that can be divided into basic and acidic solid catalysts in general have been applied to get desirable products in past decades. Na₂CO₃ or K₂CO₃ basic catalysts were reported for catalytic cracking of soybean oil and crude palm oil for biofuel.[5,15,16] The results indicate that traditional basic catalysts could reduce acid value effectively. However, inorganic salts would dissolve in biofuel, leading

to large loss of catalysts and corrosion of the equipment.[17] Xu *et al.*[18] demonstrate that calcium oxide (CaO) possesses considerable decarboxylation capacity with low solubility in biofuel. Moreover, previous work in our group[19] shows that CaO is beneficial to reducing acid value, meanwhile, decreasing the content of aromatic hydrocarbons by rupturing ringed structure. Nevertheless, CaO inhibits the pyrolysis of esters and tends to produce ketones, resulting in the high content of total oxygenated compounds.

Huge effort has been devoted to studying the effects of acidic solid catalysts such as Al₂O₃, HZSM-5 and MCM-41 on catalytic cracking of lipid for biofuel.[5,20-26] The acid sites on catalysts favor deoxygenation of fatty acids and the C–C and C=C bond cleavage of molecules, while leads unavoidably to aromatization due to the high cracking temperature and Brönsted acidity.[21,27-29] The liquid products obtained by the acidic solid catalysts contain high concentration of hydrocarbon compounds, as well as low oxygen content and viscosity. However, the pyrolytic oils with excessive acid value seriously affect the fuel properties. Otherwise, the aromatic hydrocarbons in product reduce the cetane number, and the low H/C ratio results in increasing the production of CO during burning in the engine. Furthermore, among the acidic solid catalysts, the application of Al₂O₃ shows good effect of deoxygenation with low aromatization, due to the acid sites of Al₂O₃ associated with Lewis acidity and very weak Brönsted acidity.[21] Thus, in an attempt to overcome the defects of CaO catalysts, and avoiding the production of excessive aromatic hydrocarbon by acidic solid catalysts as well, it might be a practicable method to integrate the required acid and base characters by preparing Al₂O₃/CaO composite catalyst.

Thus, catalytic cracking of soybean oil (SO) for biofuel over γ-Al₂O₃/CaO (A/C) composite catalysts has been conducted in this paper. The γ-Al₂O₃/CaO (A/C) composite catalysts were prepared by mechanical mixing with CaO as primary catalysts and γ-Al₂O₃ as additives. The main objective was to obtain hydrocarbon fuels with low acid value and oxygen content. The effects of cracking temperature and weight hourly space velocity (WHSV) were investigated according to the yield of products. Moreover, the influences of different γ-Al₂O₃/CaO composite catalysts on composition and physical-chemical properties of organic liquid product (OLP) were studied.

Experimental

Materials

CaO (AR, CAS 1305-78-8) and γ-Al₂O₃ (AR, CAS 1344-28-1) were purchased from the Aladdin Bio-Chem Technology Co., Ltd. in Shanghai, China and used as the basic and acidic solid catalysts, respectively. Soybean oil was obtained commercially without further purification and its composition and properties were determined by our previous work and listed in Tables 1 and 2, respectively.

Table 1. Fatty acid composition in soybean oil[26]

Fatty acid	Content / wt.%
Palmitic acid (C₁₆:₀)	12.5
Stearic acid (C₁₈:₀)	2.9
Oleic acid (C₁₈:₁)	34.8
Linoleic acid (C₁₈:₂)	49.1
Others	0.6

Preparation of composite catalysts

The γ-Al₂O₃/CaO composite catalysts were prepared by mechanical mixing. Firstly, powdery CaO was calcined at 800 °C in a muffle furnace due to CaO might partially hydrate and carbonate by contacting with room air. For activating CaO, the temperature of outgassing should reach 700 °C as Granados *et al.*[30] reported, and the powdery γ-Al₂O₃ was not pretreated. Secondly, powdery CaO and powdery γ-Al₂O₃ were pelleted, grinded and sieved into 20-40 mesh, respectively. Finally, the γ-Al₂O₃/CaO composite catalysts were prepared by mechanical mixing of granular CaO and granular γ-Al₂O₃. For instance, the composite catalyst containing 3.9 g of CaO and 2.1 g of γ-Al₂O₃ was denoted as 35 wt.% A/C, where A and C represented γ-Al₂O₃ and CaO, respectively, and the amount of catalyst was 6.0 g for each experiment. The other composite catalysts were denoted as 10, 20 and 50 wt.% A/C.

Catalytic cracking of soybean oil

The experiments were conducted under atmospheric pressure in a fixed-bed reactor (Figure 1). The tubular was made of stainless steel (316) with internal diameter of 16 mm and length of 380 mm. Approximately 6.0 g of

Table 2. Properties of soybean oil

Property	Densityª / (kg m⁻³)	Calorific value / (MJ kg⁻¹)	Viscosityª / cSt	C / %	H / %	O / %
Soybean oil	922	38.6	58.3	77.9	10.9	11.2

ªDetermined at 20 °C.

catalyst was placed in the middle of the reactor for each experiment. Prior to reaction, the reactor was purged of air by nitrogen, then it was heated to the desired temperature by an electric furnace. When the temperature of the catalyst bed reached a steady state, approximately 24.0 g of soybean oil was injected into reactor by a peristaltic pump at different rate of feedstock. The formula for WHSV was as follow (equation 1):

$$WHSV = \frac{r \times \rho_{so} \times 60}{m_{cat.}} \qquad (1)$$

where WHSV was weight hourly space velocity (h^{-1}), r was the rate of feedstock (mL min^{-1}), ρ_{so} was the density of soybean oil (g mL^{-1}) and $m_{cat.}$ was the amount of catalyst (g).
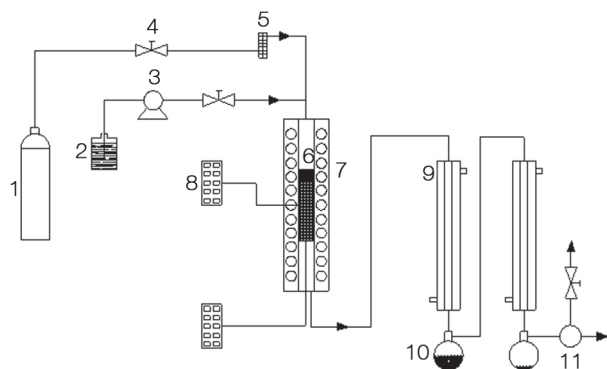

Figure 1. Schematic diagram of the experimental setup: (1) gas cylinders; (2) oil tank; (3) peristaltic pump; (4) reducing valve; (5) gas rotor flowmeter; (6) reactor; (7) heating jacket; (8) thermocouple; (9) condenser; (10) liquid product receiving bottle; (11) gas buffer bottle.

Once catalytic cracking occurred, the soybean oil (M_1) would become vapor and react with the catalysts, subsequently condensed into a liquid product (M_2) via a condenser. The liquid product consisted of the OLP (M_3) and water (M_6), after static separation, the water was obtained by a syringe, and the organic phase was collected for further analysis. The non-condensable gas was collected by a gas sampling bag. The residue (M_4) in the reactor was mainly comprised by catalyst (M_5) and solid product. Thus, the products from catalytic cracking of soybean oil included OLP, gas, solid and water. The soybean oil, OLP, water product and solid product were weight via a digital balance with the precision of 0.01 g and the mass of gas product was given by mass balance. The formula for the yield of each product was as follow (equations 2-5):

$$Yield\ (water)\% = \frac{M_6}{M_1} \times 100 \qquad (2)$$

$$Yield\ (OLP)\% = \frac{M_2 - M_6}{M_1} \times 100 \qquad (3)$$

$$Yield\ (Solid)\% = \frac{M_4 - M_5}{M_1} \times 100 \qquad (4)$$

$$Yield\ (gas)\% = \frac{M_1 - M_2 - M_4}{M_1} \times 100 \qquad (5)$$

where M_1, M_2, M_3, M_4, M_5 and M_6 represented the mass (g) of soybean oil, liquid product, organic liquid product, residue, catalyst and water, respectively.

Thermogravimetric analysis (TG, Netzsch, Germany) was applied to analyze the catalytic cracking of soybean oil with different catalysts. The catalyst (approximate 25 wt.% of soybean oil) was added to soybean oil and homogenized by stirring and ultrasonic shaking. Then, approximately 10 mg of sample was used for analysis at a temperature range of 30-700 °C with 30 °C min^{-1} heating rate. Furthermore, nitrogen (99.99%) was used as carrier gas at a constant flow rate of 40 mL min^{-1}.

The reusability of 35 wt.% A/C composite catalyst has been carried out. The used catalyst was directly calcined after reaction in a muffle furnace at 650 °C for 4 h. Then, the regenerative catalyst was applied to the catalytic cracking of soybean oil at 480 °C and 3.72 h^{-1} again. The amount of catalyst was 6.0 g.

Characterization of liquid product

The composition of OLP was determined by Agilent GC7890A-MS5975C. Separations were performed on a capillary column DB-5MS (30 m × 0.25 mm × 0.25 μm). Helium with the purity of 99.999% was used as carrier gas (1.0 mL min^{-1}), the injector temperature was 280 °C with a split ratio of 300:1. The temperature started at 50 °C (6 min), increased with the gradient of 3 °C min^{-1} to 200 °C (2 min) and 5 °C min^{-1} to 280 °C (2 min). The composition of OLP was determined on the basis of NIST library.

In addition, fuel properties were measured: acid value according to GB/T5530-2005, calorific value was determined by a IKA-C2000 basic according to GB/T384, viscosity according to GB/T5530-2005, density according to GB/T19147-2003, the carbon, hydrogen and oxygen contents of OLP were determined on a vario MACRO cube Elemental Analyser.[26]

Results and Discussion

Effects of cracking temperature and WHSV on yield of the products

The effects of cracking temperature on yield of the products were shown in Figure 2. The results illustrated

that cracking temperature played a significant role on product yield. The yield of liquid product increased from 67.4 (450 °C) to 74.9 wt.% (480 °C), and the yield of solid product was lower. However, when the temperature exceeded 480 °C, the liquid product yield decreased dramatically from 74.9 to 58.7 wt.%, on the contrary, the yield of gas product increased noticeably. It can be concluded that high temperature would promote the fracture of carbon chain, resulting in generating a large number of C_1-C_5 hydrocarbons.[31] In sum, the cracking temperature of 480 °C was suitable for biofuel production.
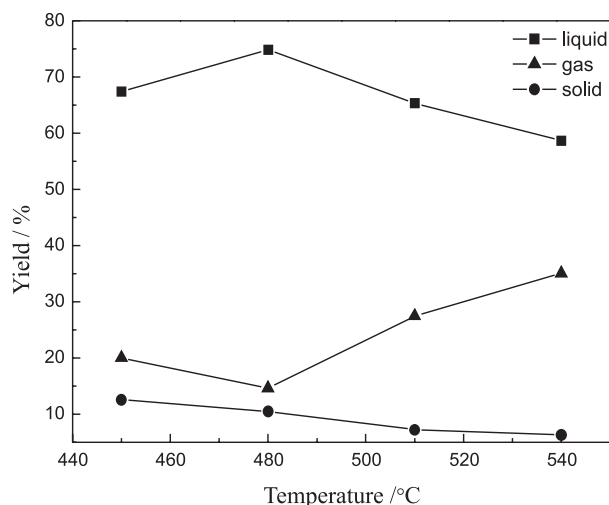

Figure 2. The effects of cracking temperature on yield of products with 35 wt.% A/C at 3.72 h⁻¹.

The relationship between products yield and WHSV at 480 °C was presented in Figure 3. The maximum yield of liquid product has been achieved at 3.72 h⁻¹ with lower yield of gas and solid product. Smaller WHSV prolonged contact time between the catalysts and the vapor of soybean oil, leading to producing more gaseous hydrocarbons such as methane, ethane and propylene.[22] Otherwise, the olefins and aromatic hydrocarbons generated from the secondary
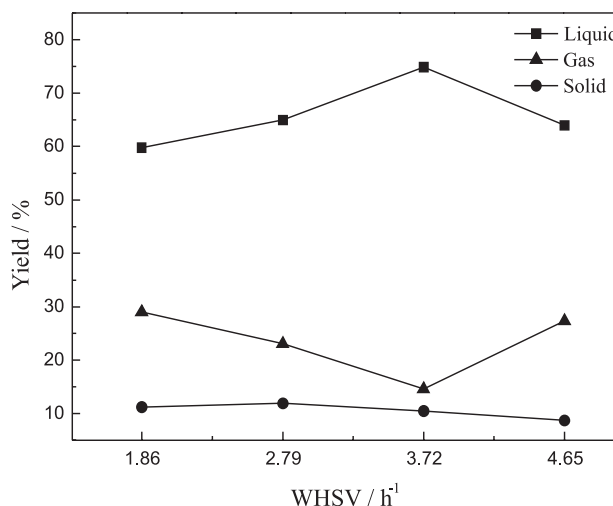

Figure 3. The effects of WHSV on yield of products with 35 wt.% A/C at 480 °C.

cracking would polymerize to form coke at smaller WHSV.[32] However, it is worth mentioning that larger WHSV would decrease the residence time of vapor in the reactor, resulting in the incomplete cracking of soybean oil. Meanwhile, the cracking temperature would be unstable due to the excessive temperature difference. As a result, the WHSV of 3.72 h⁻¹ was appropriate for catalytic cracking of soybean oil in this work.

Effects of catalysts on yield of products and distribution of OLP

The effects of different catalysts on yield of products and distribution of OLP were shown in Table 3. Higher yield of OLP (82.5 wt.%) had been obtained by thermal cracking of soybean oil, but the content of oxygenated compounds mainly composed of fatty acids was excessive. Catalytic cracking facilitated secondary cracking of soybean oil to generate hydrocarbon, thereby the physicochemical properties were remarkably better than that of thermal cracking as shown in Tables 3 and 4.

Table 3. The effects of different catalysts on yield of products and distribution of organic liquid product[a]

Comparison group	Yield of product / wt.%				Distribution of OLP / wt.%				
	OLP	Water	Solid	Gas	HC[b]	OC[c]	C / %	H / %	O / %
Thermal	82.5	2.8	0.4	14.3	46.7	53.3	78.0	11.4	10.6
γ-Al₂O₃	63.6	6.1	10.2	20.1	75.9	24.1	83.2	12.3	4.5
50 wt.% A/C	64.6	5.3	10.6	19.5	70.9	29.1	82.1	11.9	6.0
35 wt.% A/C	70.0	4.9	10.5	14.6	66.5	33.5	82.5	11.9	5.6
20 wt.% A/C	68.8	3.6	8.3	19.3	62.7	37.3	82.6	12.2	5.2
10 wt.% A/C	68.1	3.1	7.2	21.6	65.1	34.9	82.0	12.0	6.0
CaO	67.1	2.3	9.8	20.8	57.9	42.1	81.4	11.7	6.9

[a]Reaction condition: m_{SO} = 24.0 g, $m_{cat.}$ = 6.0 g, 480 °C, 3.72 h⁻¹; [b]HC represents hydrocarbon; [c]OC represents oxygenated compounds; OLP: organic liquid product; A/C: γ-Al₂O₃/CaO.

Table 4. Fuel properties

Property	Acid value / (mg KOH g^{-1})	Calorific value / (MJ kg^{-1})	Density (20 ℃) / (kg m^{-3})	Kinematic viscosity (20 ℃) / (mm^2 s^{-1})
Thermal	104.7	41.2	880.1	12.2
γ-Al$_2$O$_3$	13.5	44.2	809.8	6.3
50 wt.% A/C	8.2	44.3	810.3	7.1
35 wt.% A/C	6.7	44.2	810.6	8.0
20 wt.% A/C	4.7	43.5	828.3	6.1
10 wt.% A/C	7.0	43.9	854.6	8.5
CaO	6.3	43.4	849.9	8.4
Biodiesel[a]	0.8	38.0	860-900	1.9-6.0
Diesel[b]	–	43.0	820-860	3.0-8.0

[a]According to ASTM6751-03; [b]according to GB/T19147-2003. A/C: γ-Al$_2$O$_3$/CaO.

The content of oxygenated compounds and oxygen decreased from 53.3 to 24.1 wt.% and 10.6 to 4.5 wt.%, respectively, with γ-Al$_2$O$_3$ as catalyst, but the yield of OLP decreased sharply to 63.6 wt.% compared with thermal cracking. It is demonstrated that γ-Al$_2$O$_3$ had good deoxygenated effect and showed excessive secondary cracking. The deoxygenated effect of CaO was inferior to γ-Al$_2$O$_3$, the content of oxygenated compounds and oxygen was 42.1 and 6.9 wt.%, respectively, while the yield of OLP was slightly higher than γ-Al$_2$O$_3$. As for γ-Al$_2$O$_3$/CaO composite catalysts, by increasing the amount of γ-Al$_2$O$_3$ from 10 to 35 wt.%, the yield of OLP increased from 68.1 to 70.0 wt.%. However, the yield of OLP decreased significantly from 70.0 to 64.6 wt.% by increasing the amount of γ-Al$_2$O$_3$ from 35 to 50 wt.%. The phenomenon illustrated that appropriate amount of γ-Al$_2$O$_3$ contributed to the improvement of OLP yield. In addition, the elemental analysis also indicated that γ-Al$_2$O$_3$/CaO composite catalysts possessed better deoxygenation compared with non-catalyst or CaO. Furthermore, the yield of water increased accompanied by the increase of the amount of γ-Al$_2$O$_3$, demonstrating that the presence of acid site on γ-Al$_2$O$_3$ was beneficial to dehydration, enhancing the deoxygenated effect.[23]

Effects of catalysts on fuel properties

The purpose of this study is to obtain liquid hydrocarbon fuels that can be used in furnace or engines. Therefore, the main fuel properties of OLP gotten from thermal cracking and catalytic cracking of soybean oil were measured and shown in Table 4, and compared with biodiesel and the fuel properties specified in China as well.

It can be found from Table 4 that the acid value of OLP obtained from catalytic cracking of soybean oil was slightly higher than the specification of biodiesel and diesel fuels in China, but it was significantly lower than that of the thermal cracking. Moreover, the 20 wt.% A/C possessed the best decarboxylated effect with the acid value of 4.7 mg KOH g^{-1}. In sum, the results of calorific value, density and kinematic viscosity presented acceptable values compared to the petroleum-based fuel.

Effects of catalysts on the component of OLP

For a detailed understanding of the OLP, the components and contents of OLP were determined by gas chromatography-mass spectrometry (GC-MS) and quantified by area normalization method. The components of OLP could be classified into eight categories: alkanes, alkenes, arenes, fatty acids, esters, ketones, alcohols and ethers, which were shown in Table 5 and Figure 4. The generation process of the main products during the catalytic cracking of soybean oil over γ-Al$_2$O$_3$/CaO composite catalysts has been proposed in Scheme 1.

It is known to all that soybean oil consists of triglycerides, which are three fatty acid chains connected via ester groups to glycerol.[33] As shown in Figure 5, the fatty acid, acrolein and ketones have been produced during the primary cracking of soybean oil by breaking the ester groups at high temperature (Scheme 1, reactions 1a-1d). During the secondary cracking, fatty acids have been converted to hydrocarbons, oxygenated compounds, water, H$_2$, CO, CO$_2$, as well as coke through the chemical reactions such as decarboxylation, decarbonylation, aromatization, dehydrogenation, dehydration over γ-Al$_2$O$_3$/CaO composite catalysts.

The chemical composition of soybean oil is C$_{16:0}$ (12.5 wt.%), C$_{18:0}$ (2.9 wt.%), C$_{18:1}$ (34.8 wt.%) and C$_{18:2}$ (49.2 wt.%) fatty acid derivatives based on fatty acid

Table 5. The main components and content of OLP by thermal and catalytic cracking

Compound	Molecular formula	Relative content / wt.%			
		Thermal	$\gamma\text{-Al}_2\text{O}_3$	CaO	35 wt.% A/C
Alkane					
Octane	C_8H_{18}	1.7	2.7	2.0	2.8
Nonane	C_9H_{20}	–	1.5	–	2.9
Decane	$C_{10}H_{22}$	0.6	1.0	0.8	1.0
Undecane	$C_{11}H_{24}$	0.6	1.1	0.8	1.1
Dodecane	$C_{12}H_{26}$	3.8	1.1	6.5	1.3
Tridecane	$C_{13}H_{28}$	0.9	1.4	1.2	1.6
Tetradecane	$C_{14}H_{30}$	0.9	1.2	1.0	1.4
Pentadecane	$C_{15}H_{32}$	2.3	2.5	2.3	2.8
Heptadecane	$C_{17}H_{36}$	1.1	1.1	1.1	2.1
Alkene					
2-Octene	C_8H_{16}	2.5	1.4	2.4	2.6
1-Nonene	C_9H_{18}	2.3	1.4	2.2	3.0
1-Decene	$C_{10}H_{20}$	1.6	2.0	1.6	2.0
1-Undecene	$C_{11}H_{22}$	1.9	2.2	1.6	2.1
5-Undecene	$C_{11}H_{22}$	0.6	3.5	2.0	1.9
3-Dodecene, (Z)-	$C_{12}H_{24}$	1.5	4.3	0.3	2.1
1-Tetradecene	$C_{14}H_{28}$	3.6	2.7	4.5	3.6
7-Tetradecene	$C_{14}H_{28}$	–	2.2	–	–
1-Pentadecene	$C_{15}H_{30}$	1.6	2.0	1.6	2.3
17-Pentatriacontene	$C_{35}H_{70}$	–	–	2.6	–
Arene					
Toluene	C_7H_8	1.3	2.4	1.2	1.6
Ethylbenzene	C_8H_{10}	0.7	1.2	0.8	1.0
Benzene, butyl-	$C_{10}H_{14}$	0.4	1.1	0.6	0.8
Benzene, pentyl-	$C_{11}H_{16}$	1.2	2.0	1.1	1.6
Benzene, 1-methylbutyl-	$C_{11}H_{16}$	–	1.3	0.8	1.3
Benzene, hexyl-	$C_{12}H_{18}$	–	1.3	0.9	1.2
Benzene, 1,3-dimethylbutyl-	$C_{12}H_{18}$	–	1.2	0.9	1.1
Fatty acid					
Heptanoic acid	$C_7H_{14}O_2$	3.6	–	–	–
Octanoic acid	$C_8H_{16}O_2$	2.1	–	–	–
n-Decanoic acid	$C_{10}H_{20}O_2$	2.8	–	–	–
n-Hexadecanoic acid	$C_{16}H_{32}O_2$	8.3	–	–	0.7
cis-Vaccenic acid	$C_{18}H_{34}O_2$	6.8	–	1.8	–
Oleic acid	$C_{18}H_{34}O_2$	6.7	–	–	–
Ester					
Butyl acetate	$C_6H_{12}O_2$	3.8	–	2.3	1.9
7-Methyl-Z-tetradecen-1-ol acetate	$C_{17}H_{32}O_2$	–	–	1.2	2.1
Z,Z-3,15-Octadecadien-1-ol acetate	$C_{20}H_{36}O_2$	3.1	1.1	0.9	–
Ketone					
2-Hexanone	$C_6H_{12}O$	–	0.5	0.6	0.7
2-Heptanone	$C_7H_{14}O$	–	0.5	1.0	1.0
2-Octanone	$C_8H_{16}O$	0.7	1.3	2.3	2.2
2-Nonanone	$C_9H_{18}O$	–	0.8	1.3	1.4
3-Nonanone	$C_9H_{18}O$	–	–	0.4	0.5
2-Fluorenone	$C_{10}H_{20}O$	–	–	–	1.3
4-Fluorenone	$C_{10}H_{20}O$	–	–	0.3	–
2-Undecenone	$C_{11}H_{22}O$	–	–	2.6	–
2-Dodecone	$C_{12}H_{24}O$	–	–	2.3	–
6-Dodecone	$C_{12}H_{24}O$	–	–	0.2	–

Table 5. The main components and content of OLP by thermal and catalytic cracking (cont.)

| Compound	Molecular formula	Relative content / wt.%			
		Thermal	γ-Al$_2$O$_3$	CaO	35 wt.% A/C
Ketone					
7-Tridecanone	C$_{13}$H$_{26}$O	–	–	0.4	–
7-Hexadecanone	C$_{16}$H$_{32}$O	–	–	0.4	–
2-Heptadecanone	C$_{17}$H$_{34}$O	2.9	3.3	5.4	6.0
2-Nonadecanone	C$_{19}$H$_{38}$O	1.4	1.2	2.3	2.5
Z-5-Methyl-6-heneicosen-11-one	C$_{22}$H$_{42}$O	–	1.2	–	–
Alcohol					
E-2-Octen-1-ol	C$_8$H$_{16}$O	–	–	2.5	–
Trans, *trans*-nona-2,4-dienol	C$_9$H$_{16}$O	–	1.1	–	0.8
2-Methyl-1-undecanol	C$_{12}$H$_{26}$O	–	–	–	2.9
E-2-Hexadecacen-1-ol	C$_{16}$H$_{32}$O	1.4	2.2	0.6	–
1-Hexadecanol	C$_{16}$H$_{34}$O	–	1.7	0.3	2.1
E-2-Octadecadecen-1-ol	C$_{18}$H$_{36}$O	2.0	2.6	2.8	1.7
12-Methyl-*E*, *E*-2,13-octadecadien-1-ol	C$_{19}$H$_{36}$O	1.8	1.6	–	3.1
Behenic alcohol	C$_{22}$H$_{46}$O	–	0.4	0.6	1.5

A/C: γ-Al$_2$O$_3$/CaO.
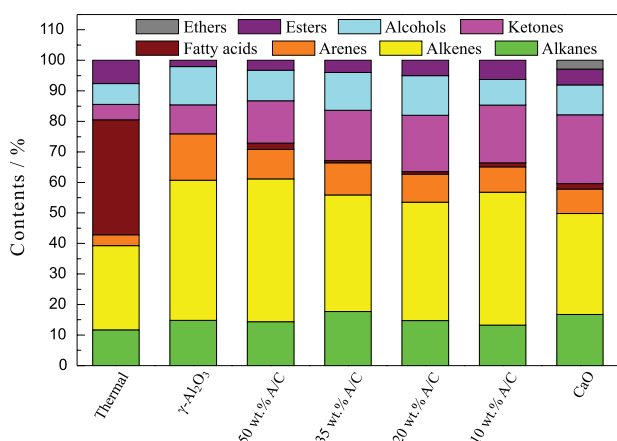
Figure 4. The effect of catalysts on component of OLP.

composition of soybean oil (Table 1). Therefore, *n*-C$_{15}$ and *n*-C$_{17}$ deoxygenated compounds have been formed by decarboxylation and decarbonylation of palmitic acid derivatives (C$_{16:0}$) and stearic acid derivatives (C$_{18:0}$). However, C$_{18}$ fatty acid derivatives are mainly composed of oleic acid derivatives (C$_{18:1}$) and linoleic acid derivatives (C$_{18:2}$), the unsaturated bond is instable at high cracking temperature and in the existence of catalyst. Thus, through β-scission of C=C bonds, various kinds of active carbenium ions were produced, followed by radical reactions such as disproportion, condensation, decarboxylation and decarbonylation to produce different hydrocarbons and oxygenated compounds.[21,29] However, catalytic cracking of soybean oil was a non-equilibrium reaction, in other words, the radical reactions were unidirectional, resulting in the complexity of the products. As can be seen from Table 5, the alkanes were mainly consisted of straight-chain

paraffin. While the composition of alkenes was complex, terminal straight-chain alkenes were the main component. Besides, methyl ketones and primary alcohols were the main composition of ketones and alcohols, respectively.

Furthermore, Figure 4 shows the effects of catalysts on components of OLP, the hydrocarbons and fatty acids were found to be the main components of the OLP produced without catalyst. The content of fatty acid reached 37.7 wt.%, demonstrating that the effect of decarboxylation was unsatisfactory by thermal cracking. The fatty acids dramatically converted into hydrocarbons via catalytic cracking, and it was also produced a certain content of oxygenated compounds such as ketones, alcohols and esters. Calcium oxide tended to convert part of fatty acids into ketones (symmetrical ketones and methyl ketones) as Zhang *et al.*[19] and Chen *et al.*[34] reported (Scheme 1, reaction 5d). The addition of γ-Al$_2$O$_3$ could change the reaction pathway mainly caused by the accessible Lewis acid sites,[28] enhancing the generation of olefins, aromatic hydrocarbons and alcohols with the decrease of ketones, thereby, the content of hydrocarbons increased significantly. For instance, the OLP obtained from catalytic cracking of soybean oil over 35 wt.% A/C compared with that of CaO, the olefins, aromatic hydrocarbons and alcohols increased from 33.1 to 38.2 wt.%, from 8.0 to 10.6 wt.% and from 9.7 to 12.3 wt.%, while ketones decreased from 22.6 to 16.5 wt.%. Noteworthy, in comparison to the CaO, the content of C$_{6-9}$ methyl ketones showed an increase in the OLP with 35 wt.% A/C as catalyst accompanied with symmetrical ketones decreasing to zero (Table 5). This might be due to the report that the γ-hydrogen transfer reaction of symmetrical ketones occurred via bonding of
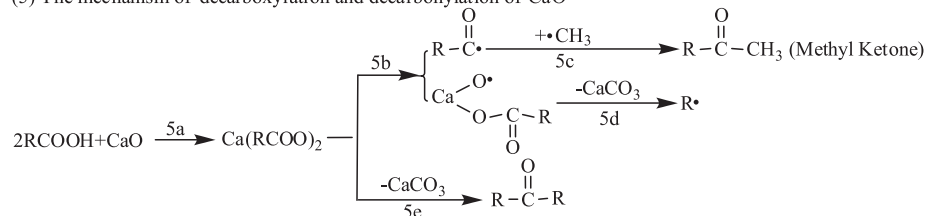
(1) Primary cracking of soybean oil
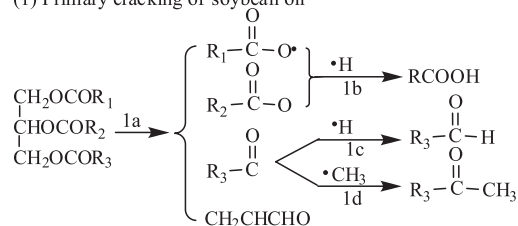
(2) Formation of CO_2, hydrocarbons, symmetrical ketones and methyl ketones
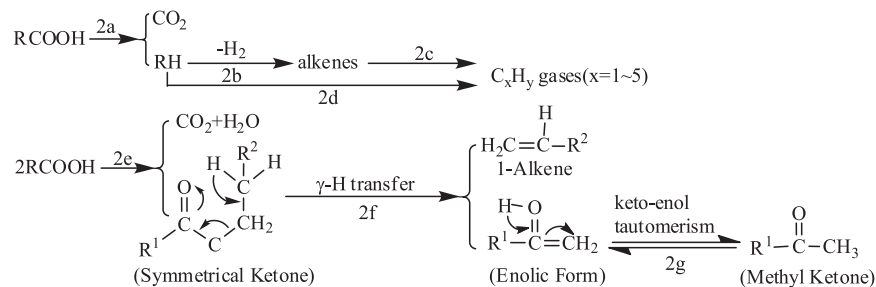
(3) Formation of CO, primary alcohols and symmetrical olefins
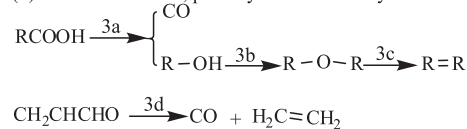
(4) Formation of aromatics, cyclic hydrocarbons and coke
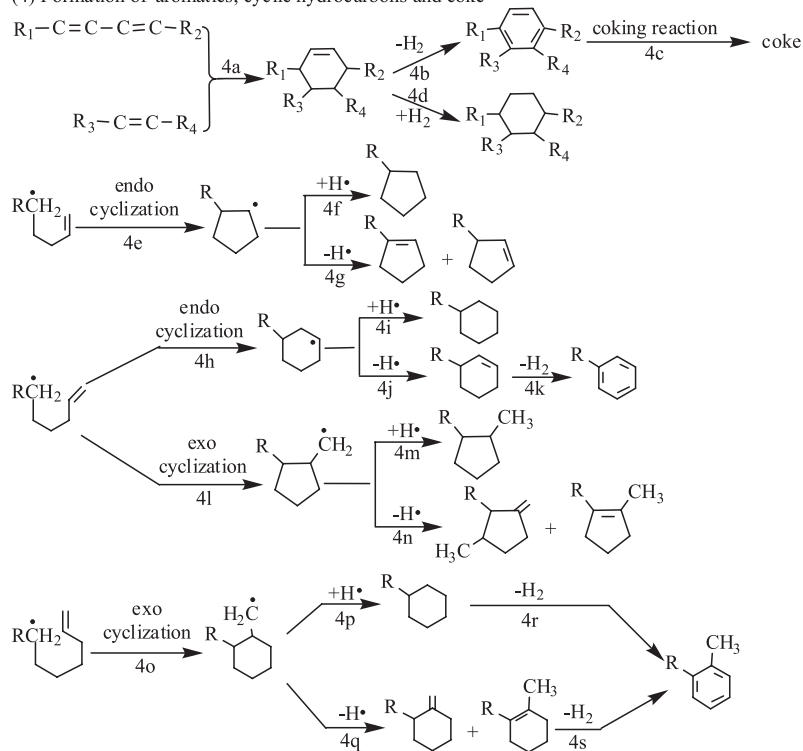
(5) The mechanism of decarboxylation and decarbonylation of CaO

Scheme 1. The generation process of the main products during the catalytic cracking of soybean oil over γ-Al₂O₃/CaO composite catalysts.
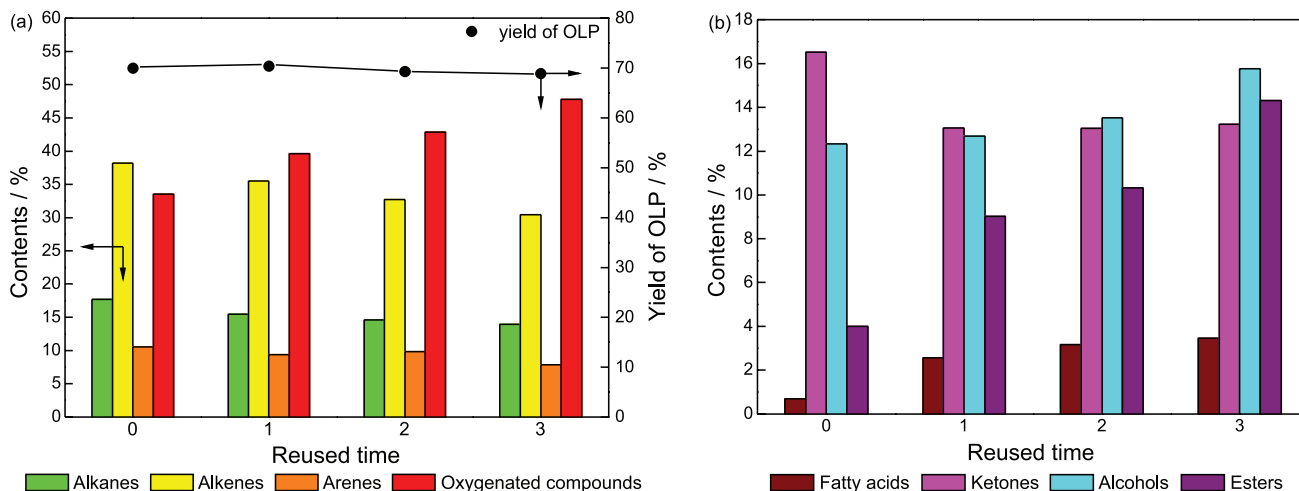
Figure 5. Stability of 35 wt.% A/C composite catalyst: (a) yield and component of OLP; (b) component of oxygenated compounds (reaction conditions: m_{SO} = 24 g, $m_{cat.}$ = 6 g, 480 °C, 3.72 h^{-1}).

oxygen to the Lewis acid sites on γ-Al$_2$O$_3$ to come into being 1-alkenes and enolic form (Scheme 1, reactions 2e-2f).[21,22] Enolic form was an intermediate product that was easy to be converted into methyl ketones by keto-enol tautomerism (Scheme 1, reaction 2g). In addition, the migration of the carbonyl group of methyl ketones would theoretically generate aldehydes, but no aldehydes have been identified, while alcohols increased. The phenomenon was attributed to aldehydes been converted into primary alcohols immediately by disproportionation during the γ-hydrogen transfer reaction. Moreover, the content of aromatic hydrocarbons increased due to the presence of accessible Lewis acid sites on γ-Al$_2$O$_3$, which were beneficial for further dehydrogenation of cyclic hydrocarbons produced during the Diels-Alder reaction (Scheme 1, reaction 4b) and free radical cyclization (Scheme 1, reactions 4k, 4r, 4s).[35]

Thermogravimetric analysis of the catalytic cracking process

It is extremely important to understand the reaction changes caused by γ-Al$_2$O$_3$/CaO composite catalysts. Thus, the TG experiments of catalytic cracking soybean oil over γ-Al$_2$O$_3$, CaO and 35 wt.% A/C were conducted, and for comparison thermal cracking of soybean oil was studied as well.

As can be seen from TG-DTG curves in Figure 6, γ-Al$_2$O$_3$/CaO composite catalysts could change the reaction pathway mainly caused by CaO, since the curves of 35 wt.% A/C composite catalyst was similar to that of CaO. The primary cracking of soybean oil (Scheme 1, reactions 1a-1d) started around 300 °C. Compared to thermal cracking of soybean oil, the maximum mass loss rate of SO + A, SO + C and SO + A/C decreased from 49.51

(430 °C) to 34.06 wt.% min^{-1} (430 °C), 40.45 (475 °C) and 35.49 wt.% min^{-1} (475 °C), respectively. That is to say, the soybean oil adsorbed on the catalysts and the secondary cracking occurred in the meantime. However, the mass loss step between 300 and 350 °C was shown in the TG curves of SO + A/C and SO + C, but not of SO and SO + A. It is illustrated that calcium oxide could promote the primary cracking of soybean oil and immediately reacted with fatty acid to yield calcium carboxylates.[35] Calcium carboxylates was instable in high temperature because the strong electron-withdrawing groups have been introduced into the carboxyl groups by saponification. Thus, in the case of SO + A/C and SO + C, the mass loss step between 415 and 510 °C could be attributed to calcium carboxylates decomposed into CaCO$_3$, ketones and hydrocarbons.[19,34] As a result, the fatty acids were remarkably converted to hydrocarbons and ketones by decarboxylation and decarbonylation (Scheme 1, reactions 5a-5e). Furthermore, the temperature of the maximum mass loss step (T_{max}) of SO + A/C and SO + C was 475 °C, higher than T_{max} of SO and SO + A (430 °C). It can be concluded that the further decomposition of fatty acid calcium into hydrocarbons and ketones needed more energy. It is worthwhile mentioning that there was a good correspondence between the T_{max} of 475 °C of SO + A/C and the suitable cracking temperature of 480 °C.

Furthermore, the mass loss step between 350 and 415 °C of SO + A/C was caused by the deoxygenation of γ-Al$_2$O$_3$. Noteworthy, the maximum mass loss rate at 475 °C of 35 wt.% A/C as catalyst compared with pure CaO decreased from 40.45 to 35.49 wt.% min^{-1}. This is because the decomposition of fatty acid calcium and the adsorption of CO$_2$ over calcium oxide lead to forming CaCO$_3$, and the increment of CaO amount promoted the
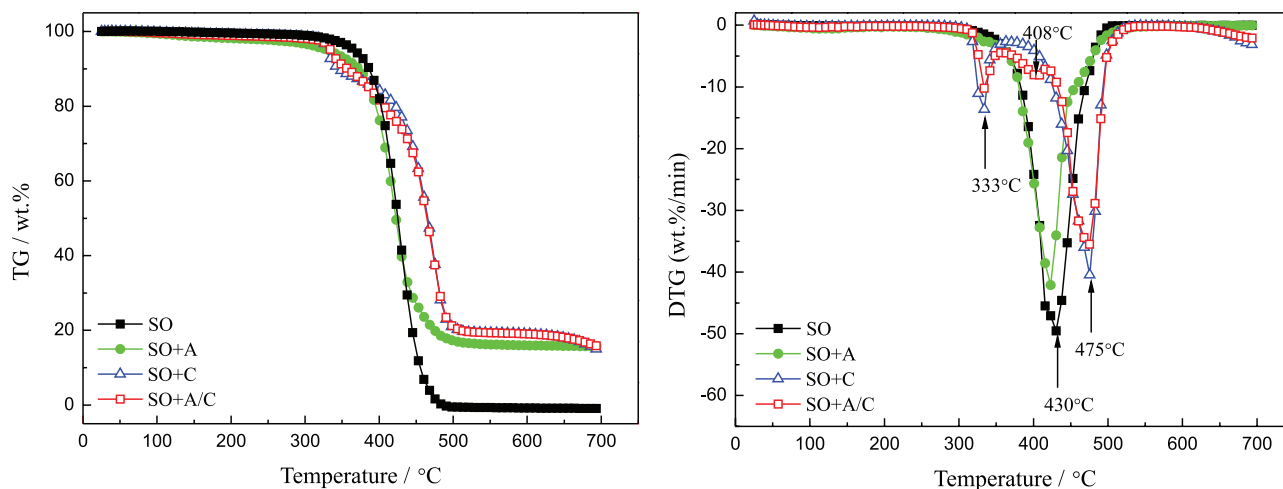
Figure 6. TG-DTG curves of soybean oil catalytic cracking over non-catalyst (SO), γ-Al₂O₃ (SO + A), CaO (SO + C) and 35 wt.% A/C (SO + A/C).

CaO carbonation reaction.[36] In addition, there was a slight weight loss at higher temperatures (575-700 °C) associated with the decomposition of $CaCO_3$.[37] It was reported that the decomposition of $CaCO_3$ occurred between 700 to 900 °C in presence of N_2 was similar to this study.[38] The decomposition shift to lower temperature in this study might be related to the presence of H_2O produced by catalytic cracking soybean oil, because water vapor could bind to the surface of $CaCO_3$ and weaken the bond energy between CaO and CO_2, thereby, promoting the decomposition rate and reducing the decomposition temperature.[39] Moreover, the above results implied that the regeneration of γ-Al₂O₃/CaO composite catalysts could be achieved by calcining the used catalysts in a steam atmosphere for reducing energy consumption and CO_2 emission.

Table 6. Characteristic parameters of soybean oil catalytic cracking

T_{max}[a] / °C	The maximum mass loss rate / (wt.% °C⁻¹)			
	SO	SO + A	SO + C	SO + A/C
333	–	–	–13.63	–10.21
408	–	–	–5.13	–8.06
430	–49.51	–34.06	–	–
475	–	–	–40.45	–35.49

[a]T_{max}: temperature of the maximum mass loss step; SO: soybean oil; SO + A: SO + γ-Al₂O₃; SO + C: SO + CaO; SO + A/C: SO + 35 wt.% A/C. A/C: γ-Al₂O₃/CaO.

Stability of γ-Al₂O₃/CaO composite catalyst

The reusability of 35 wt.% A/C composite catalyst at 480 °C and 3.72 h⁻¹ has been conducted to investigate the stability of the composite catalysts and the result was shown in Figure 5. As can be seen from Figure 5a, the OLP yield of regenerative 35 wt.% A/C reached 70.4, 69.3 and 68.9 wt.% as similar as that of fresh 35 wt.% A/C

during three cycles. However, the content of alkanes, alkenes and arenes decreased from 17.7 to 13.9 wt.%, from 38.2 to 30.4 wt.% and from 10.6 to 7.9 wt.% after three cycles, while the content of oxygenated compounds increased from 33.5 to 47.8 wt.%. The behavior could be attributed to a handful of coke and $CaCO_3$ remaining in the regenerative composite catalyst. Nevertheless, as shown in Figure 5b, the main components of oxygenated compounds were ketones, alcohols and esters, and the fatty acids content of OLP obtained by regenerative 35 wt.% A/C was remarkably lower than that of OLP from thermal cracking of soybean oil. The above results suggested that the regenerative catalyst could be applied to catalytic cracking of soybean oil with considerable catalytic effect. Anyway, it is essential to further study the regeneration of γ-Al₂O₃/CaO composite catalyst in purpose of reducing the cost of cracking production.

Conclusions

The catalytic cracking of soybean oil for biofuel was studied over the γ-Al₂O₃/CaO composite catalysts. The base sites of CaO exhibited significant fatty acid-binding performance which was beneficial to produce alkenes and ketones (symmetrical ketones and methyl ketones). The acid sites of γ-Al₂O₃ had a positive impact on generation of alkenes, arenes, methyl ketones and primary alcohols via dehydrogenation and deoxygenation. The γ-Al₂O₃/CaO composite catalysts were prepared by mechanically mixing with CaO as primary catalysts and γ-Al₂O₃ as additives. The mixed acid-base sites showed a synergic effect. The OLP yield of composite catalysts was higher than that of single CaO and single γ-Al₂O₃. The maximum yield of 70.0 wt.% have been achieved over 35 wt.% A/C. Compared with CaO, the introduction of acid sites promoted the

deoxygenation process, ketones content of OLP obtained by 35 wt.% A/C significantly decreased from 22.6 to 16.5 wt.%, while hydrocarbon content increased from 57.9 to 66.5 wt.%. Compared with γ-Al$_2$O$_3$, 35 wt.% A/C reduced the arenes content of OLP with a decrement of 4.7 wt.%. Furthermore, the fuel properties and chemical composition of the biofuel was similar to that of petroleum-based fuel, whereas free of sulfur, nitrogen and heavy metal impurities, presenting great potential for being alternative of fossil fuels. Reusability study indicated that the regenerative 35 wt.% A/C composite catalyst showed considerable reactivity after three cycles with OLP yield (> 68.9 wt.%), hydrocarbon content (> 52.2 wt.%), and fatty acids content (< 3.5 wt.%). Nevertheless, the regeneration method of γ-Al$_2$O$_3$/CaO composite catalysts could be optimized in a further work.

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