

Catalytic pyrolysis of model compounds and waste cooking oil for production of light olefins over La/ZSM-5 catalysts

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Abstract. Waste cooking oil (WCO) and its model compounds (oleic acid and methyl laurate) are catalytically pyrolyzed in a fixed-bed reactor over La modified ZSM-5 catalysts (La/ZSM-5) aiming for production of C₂-C₄ light olefins. The LaO content in catalysts was set at 0, 2, 6, 10 and 14 wt%. The gas and liquid products are analyzed. The La/ZSM-5 catalyst with 6% LaO showed higher selectivity to light olefins when WCO and methyl laurate were pyrolyzed, and olefin content was 26% for WCO and 21% for methyl laurate. The catalyst with 10% LaO showed high selectivity to light olefins (28.5%) when oleic acid was pyrolyzed. The liquid products from WCO and model compounds mainly contain esters and aromatic hydrocarbons. More esters were observed in liquid products from methyl laurate and WCO pyrolysis, indicating that it is more difficult to pyrolyze esters and WCO than oleic acid. The coked catalysts were analyzed by temperature-programmed oxidation. The result shows that graphite is the main component of coke. The conversion of WCO to light olefins potentially provides an alternative and sustainable route for production of the key petrochemicals.

1. Introduction

Light olefins such as ethylene and propylene are important basic industrial materials. Currently, light olefins are mainly produced from petroleum hydrocarbons [1]. It is well known that petroleum hydrocarbons are running low and that limits bloom in light olefin industry. Bio-oil, an alternative energy source, has been considered as a potential substitute for fossil fuels [2, 3]. Waste cooking oil (WCO) is a typical bio-oil, and millions of tons of WCO are produced in China each year. Development of new technique for effective use of WCO is one of the most pressing problems facing this country [4, 5], and helps to improve the environmental problems in China.

WCO consists mainly of triglycerides and a small amount of free fatty acids [6, 7]. Catalytic pyrolysis is a simple and efficient way to convert WCO to valuable materials. During catalytic pyrolysis process, oxygen atoms are removed by releasing H₂O, CO₂ and CO via dehydration, decarboxylation and decarbonylation mechanisms. The liquid product supplies a new material for preparation of biofuel which has similar components to that of fossil based fuels. The gas product with considerable light olefin selectivity has drawn widespread attention [8].

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2. Materials and methods

2.1. Synthesis of the La/ZSM-5 catalysts

H-type ZSM-5 zeolite (Si/Al=25) was obtained from Nankai University Catalyst Plant. (Tianjin, China). Other reagents were of analytical grade and used as received. WCO was collected from University Restaurant and used as received. La/ZSM-5 catalyst was prepared by impregnation method. $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in its desired amounts was dissolved in deionized water to form a metallic salt solution. ZSM-5 zeolite was firstly dried at 105 °C for 90 min and dispersed in the metallic salt solution. The mixed suspension was stirred at 40 °C for 30 min and 80 °C for 3 h to remove the water. The obtained solid samples were dried, tableted, and calcined at 550 °C for 5 h. The LaO content in the resulting catalysts was 2, 6, 10 and 14%, respectively. The corresponding catalyst was denoted LaO2%, LaO6%, LaO10% and LaO14%, respectively. The obtained catalysts were sieved to collect the particles passing through a 20-40 mesh screen, which were kept for the subsequent experiments.

2.2. Catalytic cracking of three kinds of oil samples

The catalytic pyrolysis experiments were carried out in a flowing fixed bed reaction system. The system was mainly composed of an inner quartz tube reactor (inner diameter: 20 mm; length 30 mm), an electric heating sleeve, a syringe located on the top of reactor (was used to inject oil samples into reactor) and a condenser. For a typical case, one gram of the sieved catalyst was used. Before the reactions, the reactor was flushed with nitrogen at a flow rate of 40 ml/min, and heated to 600 °C. 2 ml of oil samples was then pushed into the reactor by the syringe at constant speed in 2 min, and then reacted for another 2 min, thus, the total reaction time was 4 min. The formed gas and liquid products during reaction were condensed, collected and analyzed.

2.3. Product analysis

The liquid product was firstly methyl esterified according to the standard methods of GB/T 17376-2008. The components in products were analyzed by GC-MS (GC7890A; MS5975C, Agilent) equipped with HP-5MS capillary column. The inlet and detector temperature was maintained at 290 °C. The oven temperature program was set as follows: hold at 60 °C for 5 min, heated to 300 °C at 10 °C/min, and hold at this temperature for 16 min.

The gaseous hydrocarbon products were analyzed using a gas chromatography (GC, FULI-9790II) equipped with a flame ionization detector (FID). A column of HP-PLOT/Q was used. A GC equipped with a packed column (TDX-01) connected with a Residual Gas Analyzer (RGA) was used to separate and analyze CO, CO₂, N₂ and He (carrier gas). The following temperature program was used: hold at 20 °C for 4 min, heated to 240 °C at 15 °C/min, and hold at 240 °C for 15 min. The qualitative and quantitative analysis was performed using standard gases (CH₄, C₂H₄, C₂H₂, C₂H₆, C₃H₈, C₃H₄, C₃H₆, C₄H₈, C₄H₁₀, CO, CO₂, and He).

The coke on catalyst formed during pyrolysis process was analyzed using temperature-programmed oxidation (TPO) connected with RGA system. The used catalysts were temperature programmed at a rate of 10 °C/min from 100 °C to 900 °C by electric furnaces in He and O₂ mixed atmosphere (He: 40 ml/min; O₂: 2 ml/min). The released CO, CO₂ and H₂O were constantly monitored.

3. Results and discussion

3.1. Catalytic conversion of oleic acid

Figure 1 shows the product distribution for the catalytic pyrolysis of oleic acid over different La/ZSM-5 catalysts at 600 °C. GC-RGA data in Figure 1 (a) shows that the catalyst with 10% LaO had better olefins selectivity (28.5%), which is 5.45% higher than that over LaO-free catalyst. The LaO-free catalyst showed a high alkane selectivity (17.3%). A small amount of alkynes, CO and CO₂ were detected in gas products. Some other gas products are formed but cannot be identified with the present

standard gases. The gaseous product selectivity obtained over different La/ZSM-5 catalyst was summarized in Table 1.

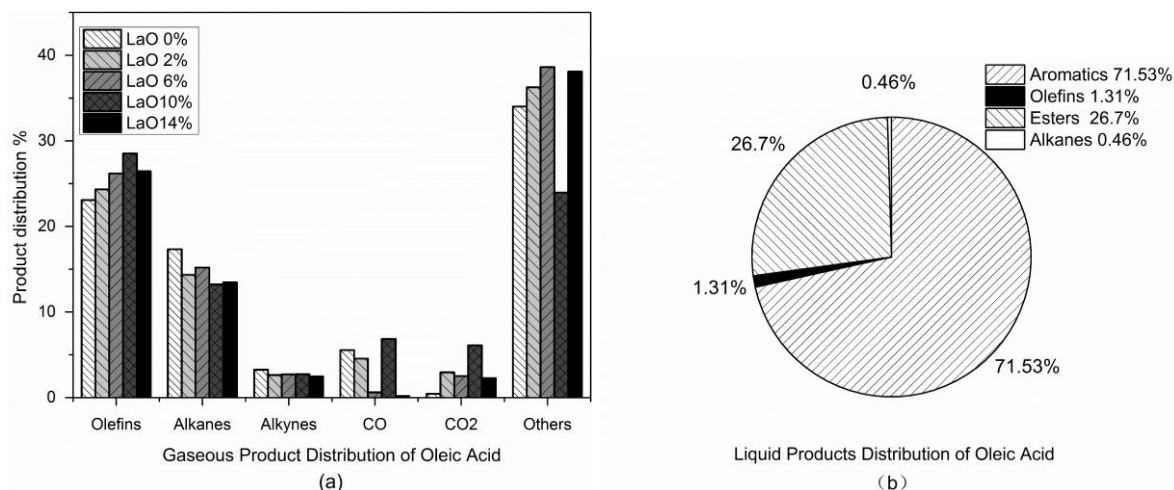


Figure 1. Gaseous (a) and liquid products distribution (b) from catalytic pyrolysis of oleic acid.

Figure 1 (b) shows the components in liquid products obtained by pyrolysis of oleic acid over LaO 10% catalyst. Liquid products contained 26.7% esters (e.g. methyl decanoate, methyl laurate, methyl palmitate, methyl stearate, etc.), 71.5% aromatic hydrocarbons (e.g. toluene, ethylbenzene, paraxylene and its derivatives, etc.) and a small amount of olefins (1.31%) and alkanes (0.46%). The results indicate that the presence of catalyst facilitates the production of light olefins. A lot of aromatic hydrocarbons as by-product were formed during catalytic conversion of oleic acid to light olefin. There is still considerable amount of oleic oil remained in liquid product, indicating the conversion reaction is incomplete. Deoxygenation of carboxyl group of oleic acid was achieved by releasing CO, CO₂ and H₂O via decarbonylation, decarboxylation and dehydration mechanisms. C₃H₈ is suggested to be an intermediate product which will form various liquid hydrocarbons through alkylation and isomerization reaction during the cracking process [9].

3.2. Catalytic conversion of methyl laurate

Figure 2 shows product distribution for catalytic pyrolysis of methyl laurate over LaO 6% catalyst. GC analysis (Figure 2 (a)) shows that LaO 6% catalyst had higher olefin selectivity (31%) and the

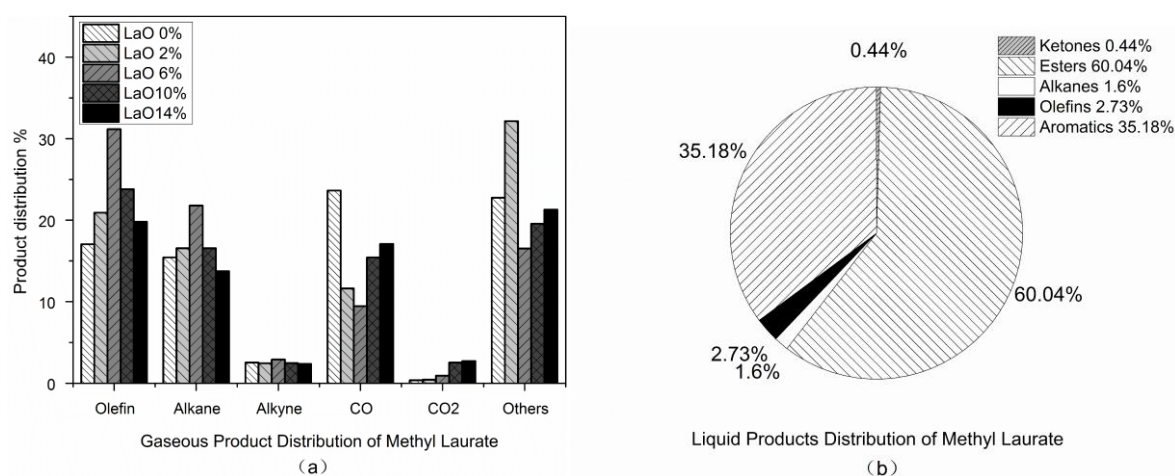


Figure 2. Gaseous (a) and liquid products distribution (b) from catalytic pyrolysis of methyl laurate.

Table 1. The components of gas products from catalytic pyrolysis of oleic acid over various La/ZSM-5 catalysts.

	Gases	The components of gas product over different catalysts (%)				
		LaO 0%	LaO 2%	LaO 6%	LaO 10%	LaO 14%
Olefin	C ₂ H ₄	9.52	9.14	10.09	11.16	10.26
	C ₃ H ₆	10.03	12.1	12.74	14.82	13.71
	n-C ₄ H ₈	3.52	3.08	3.36	2.53	2.46
	CH ₄	3.8	2.89	2.9	3.16	3.05
Alkane	C ₃ H ₈	10.24	7.08	7.94	5.4	5.89
	n-C ₄ H ₁₀	3.29	4.37	4.34	4.65	4.52
Alkyne	C ₂ H ₂	3.26	2.63	2.72	2.72	2.46
Inorganic Gas	CO	5.55	4.55	0.6	6.85	0.18
	CO ₂	0.44	2.94	2.52	6.11	2.27
	Others	33.99	36.24	38.01	23.95	38.08
C ₂ H ₄ +C ₃ H ₆ +C ₄ H ₈ Selectivity (%)		23.07	24.32	26.19	28.52	26.43
Yield (ml)						
Total gas		677	752	766	797	556
C ₂ H ₄ +C ₃ H ₆ +C ₄ H ₈		156.20	182.92	200.59	227.29	146.95

selectivity of olefins decreased as the LaO content increased. Compared with the LaO-free ZSM-5 catalyst, the olefin and alkane selectivity of LaO 6% catalyst increased by 14.11% and 6.36%, respectively. The LaO-free catalyst showed the highest CO selectivity (23.63%). The gaseous products and the product selectivity obtained at different La/ZSM-5 catalysts are summarized in Table 2. The all gas products contained a higher CO content and lower CO₂ content, indicating that deoxygenation of ester group in methyl laurate mainly followed the decarbonylation mechanism.

Figure 2 (b) shows GC-MS analysis of liquid product obtained from catalytic pyrolysis of methyl laurate over LaO 6% catalyst. As observed in Figure 2(b), the liquid product mainly contained 60.04% esters (including methyl decanoate, methyl laurate, methyl palmitate, methyl oleate and its derivatives), 35.18% aromatic hydrocarbons (including indenenes, naphthalenes, toluene, ethylbenzene, paraxylene and its derivatives, etc.), and a small amount of olefins (2.73%), alkanes (1.6%) and ketones (0.44%). There are a high content of esters remaining in liquid product, indicating an incomplete conversion reaction. Compared with oleic acid, liquid products from cracking methyl laurate contained more esters and less aromatic compounds, suggesting that esters are more difficult to be cleaved to form aromatics than aliphatic acids.

3.3. Catalytic conversion of WCO

Figure 3 shows gaseous and liquid product distribution from catalytic pyrolysis of WCO over various La/ZSM-5 catalysts. GC analysis (Figure 3(a)) shows that there was the highest olefin selectivity over LaO 6% catalyst, the content of olefins in gas product was 26%, which was 4.24% higher than that of LaO-free ZSM-5 catalyst. The selectivity to olefins decreased as LaO content increased over 6%. The selectivity to alkanes decreased as LaO content in catalysts increased. The gaseous products and the selectivity obtained over different La/ZSM-5 catalysts are summarized in Table 3. As shown in Table 3, a high selectivity to propylene (10.39%) and butylene (9.53%) was obtained, suggesting the high conversion activity of LaO 6% catalyst.

Table 2. The composition of gas products from catalytic pyrolysis of methyl laurate over various La/ZSM-5 catalysts

Gas		The composition of gas products obtained with various catalysts (%)				
		LaO 0%	LaO 2%	LaO 6%	LaO 10%	LaO 14%
Olefin	C ₂ H ₄	5.91	7.28	10.97	8.24	6.9
	C ₃ H ₆	7.89	9.82	15.18	12.18	10.19
	n-C ₄ H ₈	3.25	3.82	5.01	3.37	2.72
Alkane	CH ₄	3.35	3.01	3.94	3.21	3.14
	C ₃ H ₈	8.81	9.66	12.07	8.81	6.7
	n-C ₄ H ₁₀	3.26	3.88	5.78	4.54	3.89
Alkyne	C ₂ H ₂	2.54	2.45	2.9	2.46	2.36
Inorganic	CO	23.63	11.63	9.45	15.43	17.09
Gas	CO ₂	0.36	0.43	0.92	2.54	2.71
	Others	22.75	32.14	16.53	19.57	21.3
C ₂ H ₄ +C ₃ H ₆ +C ₄ H ₈		17.05	20.91	31.16	23.8	19.8
Selectivity (%)						
Yield (ml)						
Total gas		507	582	625	592	530
C ₂ H ₄ +C ₃ H ₆ +C ₄ H ₈		86.44	121.73	194.74	140.90	104.96

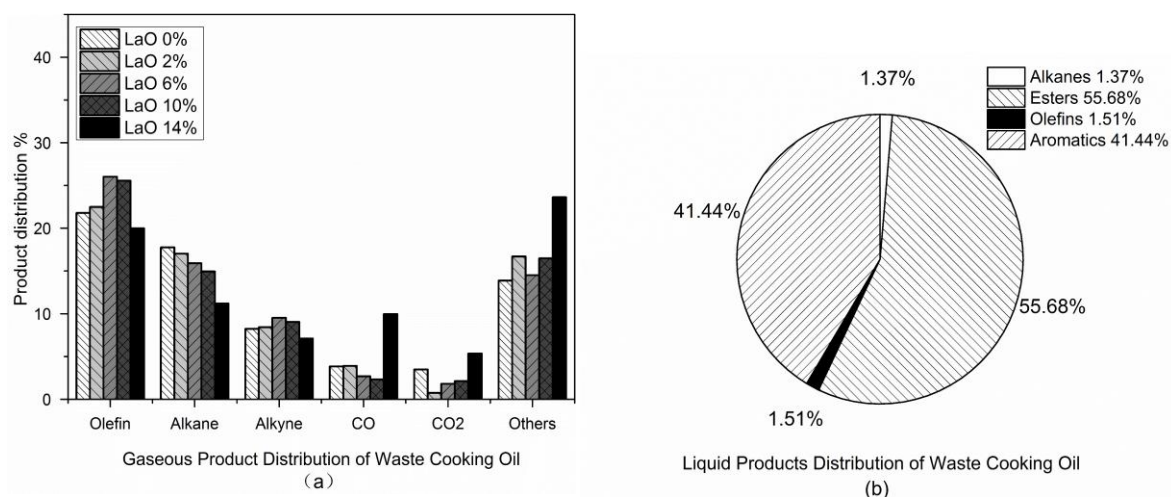
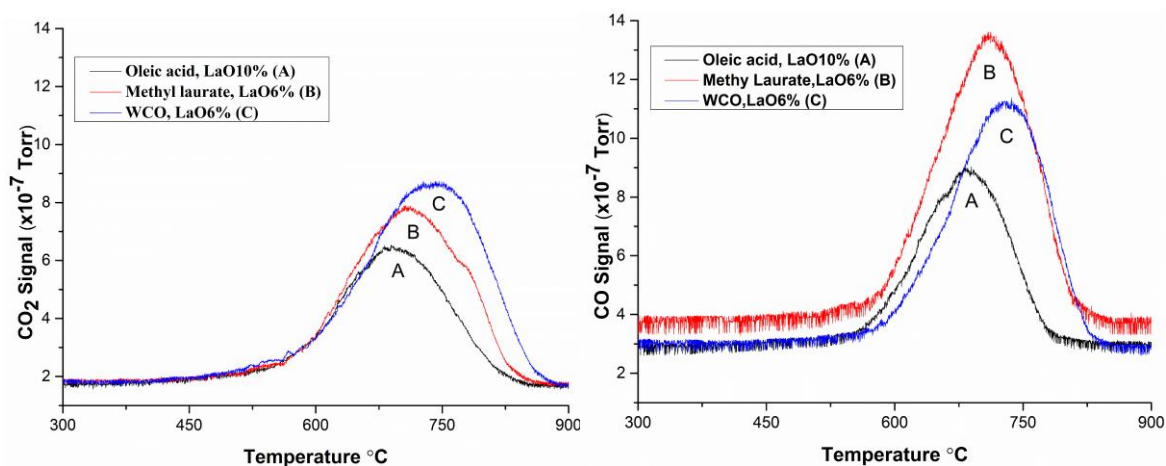
**Figure 3.** Gaseous (a) and liquid product (b) distributions from catalytic pyrolysis of WCO.

Figure 3 (b) shows the result of GC-MS analysis of liquid product from catalytic pyrolysis of WCO over LaO 6% catalyst. It was found from Figure 3(b) that the liquid products mainly contained 55.68% esters (including methyl caprate, methyl enanthate, dodecanoic acid methyl ester, methyl tetradecanoate, etc.), 41.44% aromatic hydrocarbons (including indenenes, naphthalenes, toluene, ethylbenzene, paraxylene and its derivatives, etc.), and a small amount of olefins (1.51%) and alkanes (1.37%). The composition of liquid product was similar to that from catalytic pyrolysis of methyl laurate, and there were a lot of esters remaining in products, indicating a lower conversion of WCO. By comparison, it is more difficult to pyrolyze WCO and methyl laurate than aliphatic acids by using present catalysts.

Table 3. The composition of gas products from catalytic pyrolysis of WCO at various LaO.

Gases		The composition of gas products over various catalysts (%)				
		LaO 0%	LaO 2%	LaO 6%	LaO 10%	LaO 14%
Olefin	C ₂ H ₄	3.84	3.38	3.37	2.86	2.5
	C ₃ H ₆	8.92	9.13	10.39	9.84	7.62
	n-C ₄ H ₈	8.24	8.42	9.53	9.04	7.1
Alkane	CH ₄	9.35	9.8	12.57	12.47	10.4
	C ₃ H ₈	10.68	10.38	8.38	7.77	5.09
	n-C ₄ H ₁₀	3.52	3.55	3.06	3.26	1.98
Alkyne	C ₂ H ₂	3.24	3.27	4.16	4.31	3.61
Inorganic	CO	3.84	3.9	2.69	2.32	9.97
Gas	CO ₂	3.49	0.74	1.81	2.12	5.34
Others		13.86	16.71	14.51	16.48	23.63
C ₂ H ₄ +C ₃ H ₆ +C ₄ H ₈		21.78	22.48	26.02	25.57	20
Selectivity (%)						
Yield (ml)						
Total gas		767	792	822	792	547
C ₂ H ₄ +C ₃ H ₆ +C ₄ H ₈		167.06	178.06	213.87	202.49	109.39

**Figure 4.** TPO profiles of the three catalysts after cracking of the three oils.

3.4. Coke analysis

The coke deposits and carbon content on catalysts formed during catalytic pyrolysis reactions were analyzed via TPO-RGA system. The result is shown in Figure 4. The order of the temperature corresponding to peak height (Tp) in TPO curves of three oil samples (Figures 4(a) and (b)) are: WCO > methyl laurate > oleic acid. The order of the total amount of CO and CO₂ are: methyl laurate > WCO > oleic acid. These results suggest that more graphite-type carbon with high thermal-stable structure was formed in catalytic pyrolysis process of WCO and methyl laurate. The Tp of coke deposited on LaO6% catalyst (740 °C) shifted towards lower temperatures (670 °C) as the LaO content increased to 10%, indicating that La addition likely causes the decrease in the acidic properties of catalysts. CO and CO₂ are formed due to incomplete and complete oxidation of the deposited carbon, respectively. H₂O and organic gas had not been detected in TPO curves, indicating few H

content of coke. These results suggest that graphite is likely the main component in the coke deposited on present catalysts [10, 11].

4. Conclusions

Light olefins were produced from catalytic pyrolysis of WCO and its model compounds. A high selectivity of light olefins up to 26% was obtained by catalytic pyrolysis of WCO over La/ZSM-5 catalyst with 6% LaO content. The obtained light olefins mainly contained propylene (10.39%) and butylene (9.53%). The liquid composition of WCO pyrolysis product remained a lot of esters (55.68%) which was similar to that from catalytic pyrolysis of methyl laurate, indicating a lower conversion of WCO and methyl laurate by using present catalysts. Graphite is the main component in the coke deposited on present catalysts. In the future research, the effects of several parameters such as reaction temperature and liquid hourly space velocity will be investigated to further improve the light olefins yield. The mass balance analysis of reactants will be conducted and the characteristics of the catalysts will be examined in the future work.

Acknowledgements

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