

**CHAPTER VI**  
**CATALYTIC DEOXYGENATION OF**  
**OLEIC ACID OVER  $Ce_{1-x}Zr_xO_2$  CATALYSTS**

**6.1 Abstract**

In this study, the catalytic deoxygenation of oleic acid ( $C_{17}H_{33}COOH$ ) was investigated over  $Ce_{1-x}Zr_xO_2$  mixed oxide catalysts. The results showed that the deoxygenation of oleic acid can be achieved via direct decarboxylation resulting in  $C_{17}$ -hydrocarbons and  $CO_2$ . The  $Ce_{0.75}Zr_{0.25}O_2$  catalyst exhibits the highest activity. The extent of the activity is related to its degree of reducibility. The evidence of CO indicated that the decarbonylation reaction occurs simultaneously. This reaction is more pronounced over more reducible catalyst at the temperature higher than  $375^\circ C$  as found in the case of  $Ce_{0.75}Zr_{0.25}O_2$  and  $CeO_2$ . Kinetic studies showed that the rate of the catalytic deoxygenation of oleic acid over  $Ce_{0.75}Zr_{0.25}O_2$  catalyst follows the first order kinetic model and the calculated activation energy was reported at ca.  $23 \text{ kcal mol}^{-1}$ .

**6.2 Introduction**

Pyrolysis of biomass is found to be the promising technique for energy production. The pyrolytic liquid or bio-oil was considered to be high potential resource for applying as a diesel fuel and diesel fuel additives after treating with proper upgrading methods [1, 2]. One of difficulties for using of bio-oil as a fuel is the high portion of carboxylic acids in the bio-oil which is defined as an oxygenated compound (up to 36 wt.%) [3]. Carboxylic acids make liquid very corrosive and extremely severe at elevated temperature. Moreover, the high oxygen content leads to the lower energy density up to 50% comparing to the conventional fuel and also immiscibility problem with hydrocarbon fuel. In addition, the strong acidity of bio-oils makes them extremely unstable [4]. Hence, deoxygenation of the bio-oil is essential.

There are several techniques for upgrading the bio-oil by removal of oxygen atoms from the oxygen containing compounds [4]. Among all techniques, the catalytic cracking is regarded as the cheapest route, but facing a severe coking (8-25 wt.%) problem and non-selective liquid products were obtained [4-7]. On the other hand, the

hydrotreating process requires complicated equipments, superior techniques and excess of hydrogen [4]. Therefore, the catalytic deoxygenation is a promising candidate route due to simple equipment requirement, ease of operation at low pressure condition and the reasonable cost of reacting agent.

A part from the operational advantages, high product selectivity toward long chain hydrocarbons was obtained. The selective production of diesel fuel hydrocarbons from renewable vegetable-based feeds was recently reported, where the deoxygenation was performed by the selective removal of the carboxyl group [8].

The catalytic deoxygenation of carboxylic acid has been studied over both non-reducible and reducible catalysts. The disadvantage of using the non-reducible catalysts such as activated alumina is coke formation. Amount of coke was increased as a function of the carbon number of acids from 10.3 wt.% (for C<sub>4</sub> acids) to 25.6 wt.% (for C<sub>12</sub> acids). Moreover, various non-selective products resulting from the ketonization reaction were also obtained [9].

The catalytic deoxygenation of acetic acid [10] and benzoic acid [11, 12], have been studied over several types of the metal-oxide catalysts. A great number of metal-oxides were tested and a correlation between reducibility and catalytic behavior was found [13]. CeO<sub>2</sub>, ZnO and ZrO<sub>2</sub> exhibit a good catalytic performance and highly selective reduction of benzoic acid to benzaldehyde at low temperature ( $T < 375^{\circ}\text{C}$ ), especially CeO<sub>2</sub>. At higher temperature ( $T > 375^{\circ}\text{C}$ ), the obtained benzaldehyde was further decomposed to benzene and toluene by forming CO<sub>2</sub> and CO as major components in gas phase [14]. ZrO<sub>2</sub> was also reported to promote the decarboxylation of stearic acid resulting in C<sub>16</sub>-hydrocarbons and CO<sub>2</sub> under the supercritical water. The addition of KOH into ZrO<sub>2</sub> was found to promote the decarboxylation of stearic acid to C<sub>17</sub>-hydrocarbons and CO<sub>2</sub> without breaking of long chain hydrocarbons [15]. Recently, the addition of Zr atom into the CeO<sub>2</sub> lattice can increase the thermal stability and reducibility of the catalysts and it has also shown to be active in several other reactions, including partial oxidation [16], selective dehydration [17] and esterification [18]. Therefore, it might be expected to increase the deoxygenation activity with less coke formation [19, 20]. Hence, the aim of this contribution is to investigate the catalytic deoxygenation of oleic acid over the reducible catalysts (Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> mixed oxide catalysts). The kinetic analysis over the most active catalyst was purposed.

## 6.3 Materials and methods

### 6.3.1 Catalysts preparation and characterizations

Ceria-zirconia mixed metal oxide catalysts were prepared via urea hydrolysis technique. The 0.1 M of each metal salt solutions were prepared from cerium nitrate ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (99.0%), Fluka), and zirconium oxychloride ( $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  (99.0%), Fluka) using as sources of Ce and Zr, respectively. The ratio of Ce/Zr in the catalyst composition was altered by varying the volume of the solution to obtain the desired composition of catalyst. The synthesis procedure and characteristics of catalysts has been reported elsewhere [19]. The BET surface areas of the catalysts were in the range of 78-122  $\text{m}^2 \text{g}^{-1}$ .

### 6.3.2 Activity test

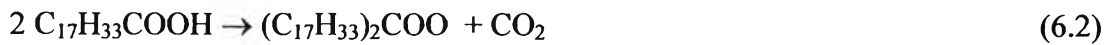
Catalytic activity tests for the decarboxylation of oleic acid ( $\text{C}_{17}\text{H}_{33}\text{COOH}$ ) were carried out in a stainless steel packed bed reactor (I.D. 3/8 in.). The amount of catalyst (0.10-0.70 g) was packed between the two layers of the glass wool. The reactor was placed in an electrical furnace equipped with K-type thermocouples. The temperature of the catalyst bed was monitored and controlled by Shinko temperature controllers. The reaction temperature was carried out in the range of 325-425°C. Oleic acid was fed at 1.0-5.0  $\text{ml h}^{-1}$  by the ISCO model 260D high pressure liquid syringe pump with the dilute of nitrogen gas. The flow rate of nitrogen was kept at 50  $\text{ml min}^{-1}$  by Brooks mass flow controllers. The outlet stream was condensed by two condensing traps that kept at room temperature and immersed in the ice/acetone bath. Exit gases were online chromatographically analyzed for CO and  $\text{CO}_2$  by Shimadzu 8A equipped with a TCD detector. The condensed liquids were off-line analyzed using Thermofinigan Trace GC 2000 gas chromatograph fitted with the FID.

The kinetic studies were carried out in the same system as mentioned above. By varying mass of catalyst, the kinetic parameters (i.e., activation energy and pre-exponential factor) were evaluated.

## 6.4 Results and discussions

### 6.4.1 Catalytic deoxygenation of oleic acid

The results showed that CO and CO<sub>2</sub> were the major gas compositions with the trace of CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> for the catalytic deoxygenation of oleic acid at temperatures above 425°C, regardless of mixed oxides used. Similar findings were reported in the studied of decarboxylation of naphthenic acid [21] and stearic acid [8, 22]. The presence of CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> is due to the thermal cracking and accounted for 1.3% of the total gas yield in our study. It was found that yields of both CO, Fig 6.1(a), and CO<sub>2</sub>, Fig 6.1(b), gradually increased with an increasing temperature (325-385°C) and rapidly increased at temperature above 385°C. It was reported that CO<sub>2</sub> was produced from decarboxylation and ketonization reactions [21-24] while CO was produced from decarbonylation reaction [8]. The decarboxylation, ketonization and decarbonylation of oleic acid were proposed in Eq. (6.1), (6.2) and (6.3), respectively [22].



The oleic acid conversion ( $x$ ) was calculated from the CO and CO<sub>2</sub> yields and can be represented by Eq. (6.4)

$$\text{Oleic acid conversion } (x) = \frac{(y_{\text{CO}} + y_{\text{CO}_2})F_T}{F_{\text{OA}}} \times 100 \quad (6.4)$$

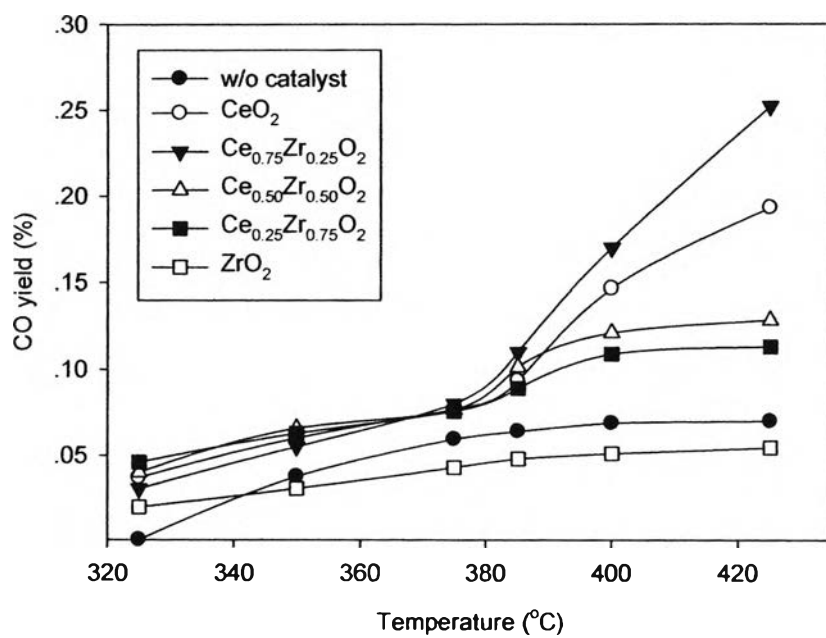
where  $y_{\text{CO}}$ ,  $y_{\text{CO}_2}$ ,  $F_T$  and  $F_{\text{OA}}$  were yield of CO, CO<sub>2</sub>, total flow rate (mol min<sup>-1</sup>) and inlet flow rate of oleic acid (mol min<sup>-1</sup>), respectively

It was found that the catalytic activity for the deoxygenation of oleic acid was in the order of Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> > CeO<sub>2</sub> > Ce<sub>0.50</sub>Zr<sub>0.50</sub>O<sub>2</sub> ≈ Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub> ≈ ZrO<sub>2</sub> (Figure 6.2) which are found to relate to the redox properties of the mixed oxide catalysts. It has been reported that the reducibility of the catalysts declines in the order: Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> > CeO<sub>2</sub> > Ce<sub>0.50</sub>Zr<sub>0.50</sub>O<sub>2</sub> > Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub> as shown in Figure 6.3.

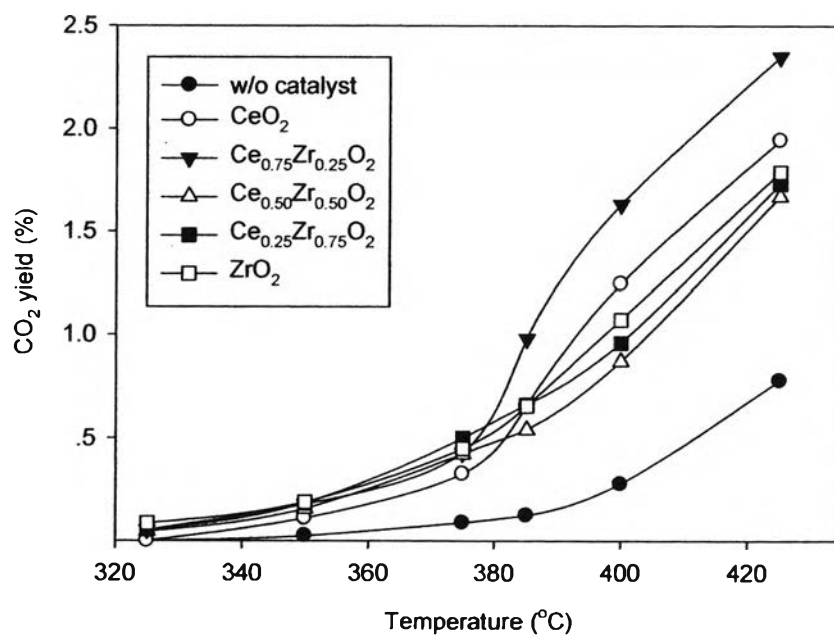
The results also showed that liquid products derived from the deoxygenation of oleic acid, mainly consist of hydrocarbons ranging from C<sub>6</sub>-C<sub>18</sub> with the high selectivity toward C<sub>17</sub>-hydrocarbons for all studies as depicted in Figure 6.4. These suggested that catalysts preferentially promote the deoxygenation via direct decarboxylation, Eq. (6.1). The absence of symmetric ketones indicated the insignificant of the ketonization reaction during the course of the catalytic deoxygenation of oleic acid.

The plot of CO<sub>2</sub>/CO ratio against the reaction temperature was applied for the indication of dominating reaction over the Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> catalysts as shown in Figure 6.5. The results showed that the CO<sub>2</sub>/CO ratio is greater than 1 for all cases suggesting that the direct decarboxylation reaction was the dominating reaction for both non-catalytic and catalytic deoxygenation. The similar findings were found in the deoxygenation of stearic acid over Pd/C [8], sulfated zirconia [23] and activated alumina [24]. The CO<sub>2</sub>/CO ratio monotonically increases as a function of reaction temperature for all catalysts except for Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> and CeO<sub>2</sub>. The CO<sub>2</sub>/CO ratios of Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> and CeO<sub>2</sub> catalysts were relatively constant after 385°C. This might be resulted from the decomposition of the adsorbed oleic acid through the decarbonylation reaction. The oleic acid could be adsorbed by filling the vacancy with the oxygen in the carboxyl group resulting in the adsorbed layer and then decomposed to form C<sub>17</sub>-hydrocarbons and CO at the temperature higher than 375°C. The similar finding was found in the case of deoxygenation of benzoic acid [14]. Among all catalysts, Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> catalyst was found to shows the highest yield of the C<sub>17</sub>-hydrocarbons, approximately 36 wt%. This is related to the reducibility of Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> catalyst providing the higher oxygen vacancy site for the adsorption of oleic acid molecule.

For less reducible catalysts, CO production was insignificant due to lower oxygen vacancy sites.

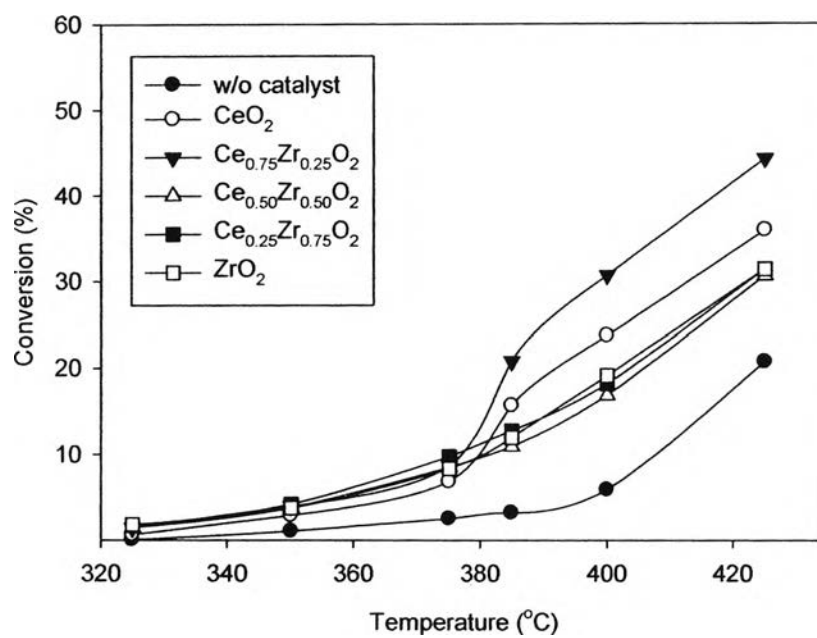


(a)

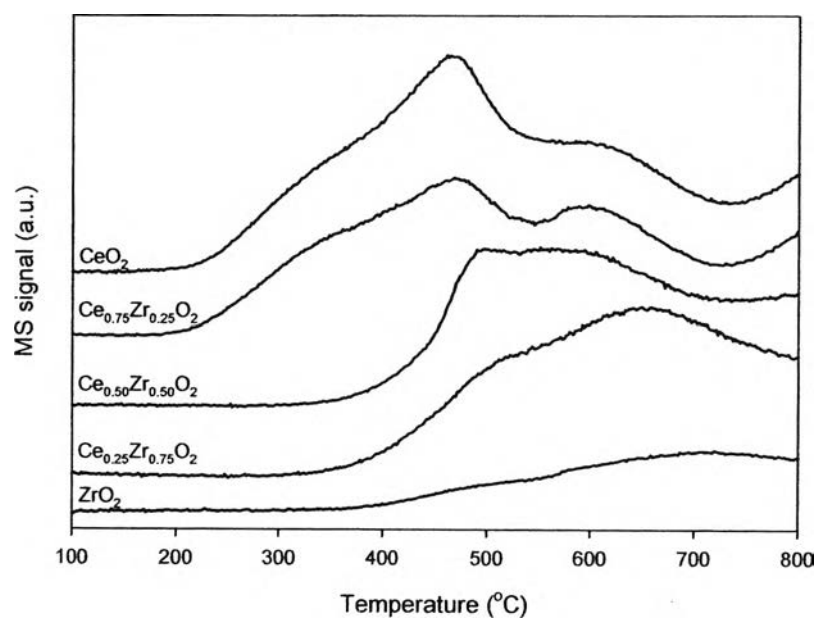


(b)

**Figure 6.1** The yield of (a) CO and (b)  $\text{CO}_2$  as a function of reaction temperature

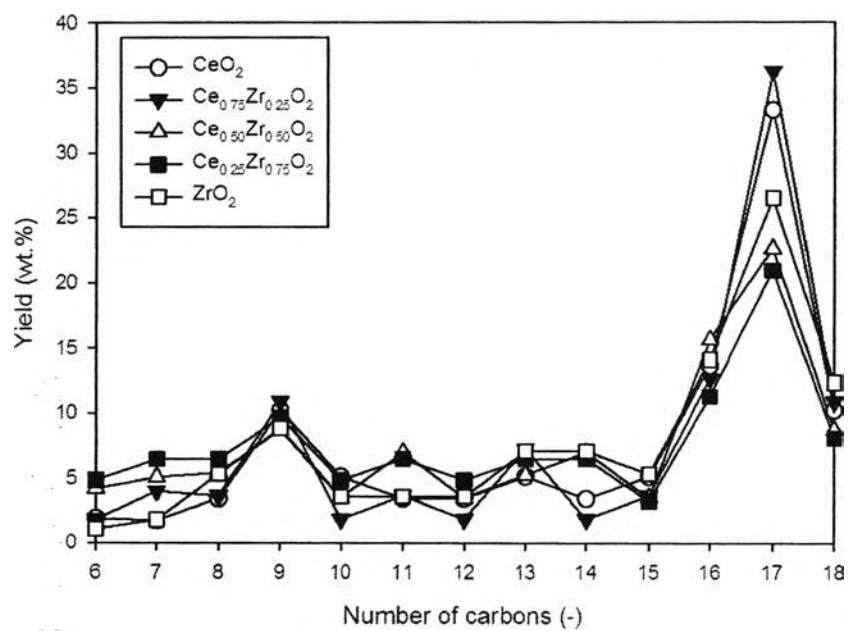


**Figure 6.2** Effects of temperature on oleic acid conversion for the deoxygenation of oleic acid over ceria-zirconia catalysts and non-catalytic system

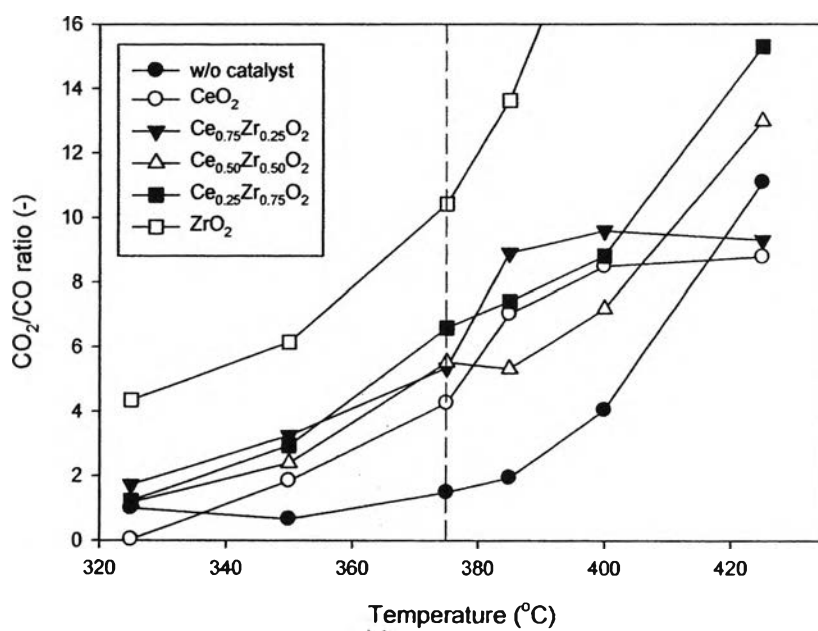


**Figure 6.3** CO-TPR profiles of the  $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$  catalysts





**Figure 6.4** The distribution of the liquid product obtained from the deoxygenation of oleic acid under nitrogen atmosphere at 385°C



**Figure 6.5** CO<sub>2</sub>/CO ratio as a function of reaction temperature for the deoxygenation of oleic acid over ceria-zirconia catalysts

#### 6.4.2 Kinetic Studies

The kinetic studies were conducted on the most active catalyst,  $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ , for the deoxygenation of oleic acid. The experiments were conducted at three different temperatures (375, 385, and 400°C) with four different mass of catalysts (0.1, 0.3, 0.5 and 0.7 g) and the plot between acid conversion and  $m/F_0$  ratio were presented in Figure 6.6. The acid conversions in the cases of without catalysts were included in the plot. The assumptions and simplifications were made to minimize heat and mass transfer effects as mentioned elsewhere [24].

To determine the reaction order by the integral rate method, the reaction order has to be presumed for integrating the differential equation. After integration, the kinetic representation for the hypothesis of each reaction order,  $n = 0, 1.0, 1.5$  and  $2.0$ , can be written in Eq. (6.5), (6.6), (6.7) and (6.8), respectively.

$$r_0 = \frac{F_0}{m} x \quad ; n = 0 \quad (6.5)$$

$$r_0 = -\frac{F_0}{m} \ln(1-x) \quad ; n = 1.0 \quad (6.6)$$

$$r_0 = -\frac{F_0}{m} \frac{2}{(1-x)^{1/2}} \quad ; n = 1.5 \quad (6.7)$$

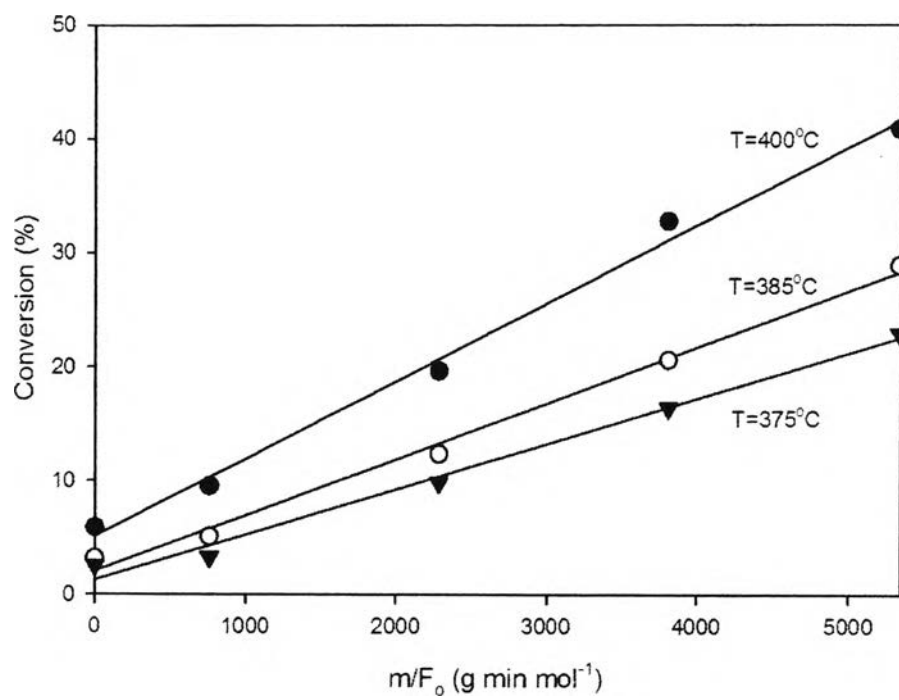
$$r_0 = \frac{F_0}{m} \frac{x}{(1-x)} \quad ; n = 2.0 \quad (6.8)$$

where  $r_0$ ,  $F_0$ ,  $m$  and  $x$  were reaction rate, total gas flow rate, mass of catalysts and acid conversion, respectively. The plot  $x$ ,  $\ln(1-x)$ ,  $2/(1-x)^{1/2}$  and  $x/(1-x)$  versus  $m/F_0$  were made for  $n = 0, 1.0, 1.5$  and  $2.0$ , respectively. If the plot yields the straight line with the regression coefficient greater than 0.995, it can be concluded that the reaction order which we presumed was the order of reaction. For example, the plot for  $n = 1.0$  (at

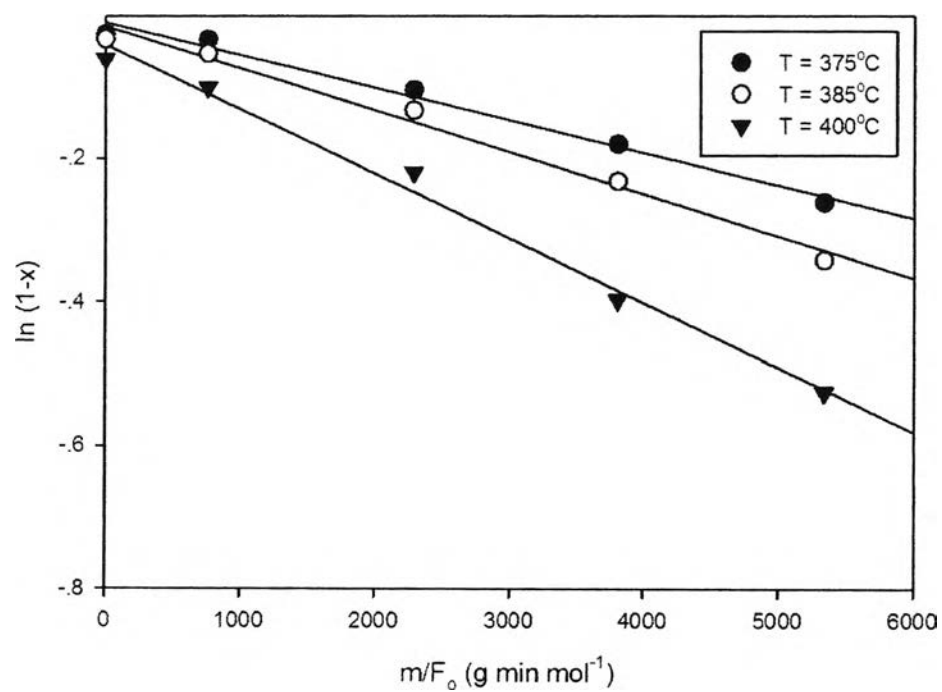
different temperatures) showed the straight line with the regression coefficient greater than 0.995 for all temperature studied as illustrated in Figure 6.7. Therefore, it can be concluded that the first order was reasonable. All values of the rate parameters obtained from the plot were shown in Table 1. Moreover, the reaction order determination by the power-law kinetic model was also applied. The plot of  $\ln(-r_o)$  versus  $\ln(C_o)$  was shown in Figure 6.8. Then, the reaction order was determined from the slope of the line. The results showed that the reaction order was also 1.0 for all temperatures.

The reaction order of oleic acid deoxygenation was the first order which was similar to the catalytic decarboxylation of octanoic acid [24] and mixture of used palm oil and palm oil fatty acids [26] while the reaction order of the deoxygenation of used vegetable oil was reported to be second order [23].

The reaction rate ( $r_o$ ) were calculated by the slope of the plot of  $n = 1.0$  using Eq. (6.6). Then, the reaction rate constants were calculated by  $k = r_o/c_o$ . In this case  $c_o$  was  $2.62 \times 10^{-3} \text{ mol l}^{-1}$ . According to the equation  $k = A \exp(-E_a/RT)$ , the activation energy and pre-exponential factor were obtained from the slope and interception, respectively, of the plot of  $\ln k$  versus  $1/T$  as shown in Figure 6.9. The estimated activation energy was  $22.8 \text{ kcal mol}^{-1}$  and the pre-exponential factor was  $1.32 \times 10^9 \text{ l h}^{-1} \text{ g}_{\text{CAT}}^{-1}$ . The activation energy was found to be higher than the activation energy of decarboxylation of octanoic acid ( $16.97 \text{ kcal mol}^{-1}$ ) [24]. This might be due to oleic acid has higher molecular mass than octanoic acid.



**Figure 6.6** The plot of conversion against  $m/F_0$  ratio



**Figure 6.7** The plot of  $\ln(1-x)$  vs  $m/F_o$  (hypothesis of  $n = 1.0$ )

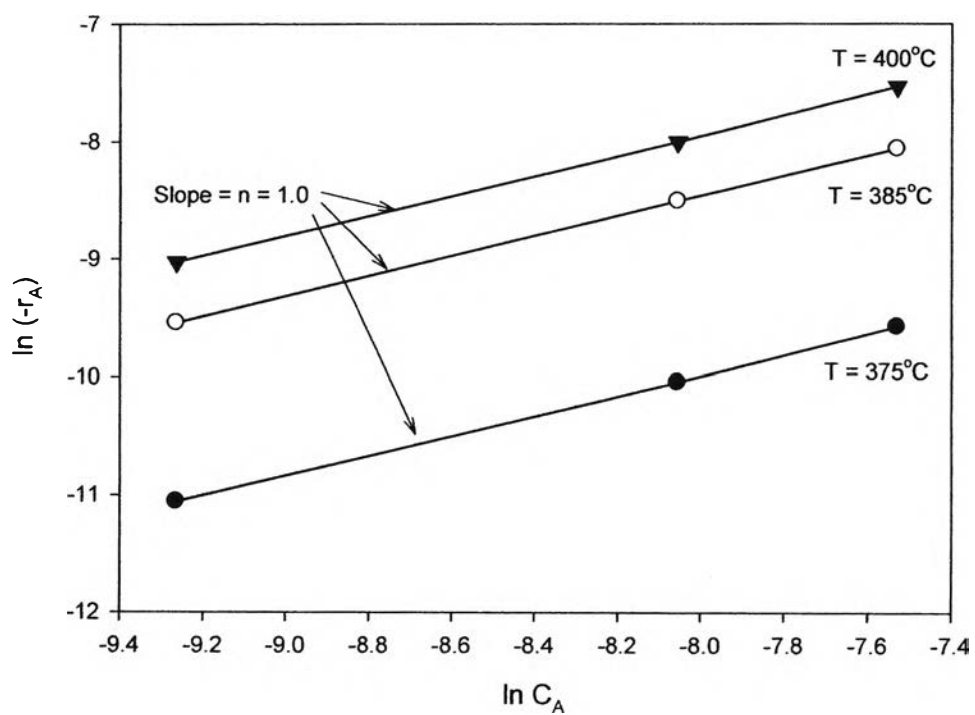
**Table 6.1** The initial rate ( $r_o$ ) and rate constant ( $k$ ) derived from the deoxygenation of oleic acid

Reaction order	Simplified rate expression	Temperature (K)	Parameter		$R^2$
			$r_o^a (\times 10^{-6})$	$k^b (\times 10^2)$	
n = 0	$r_o = \frac{F_o}{m} x$	648	0.338	1.290	0.9576
		658	0.847	3.233	0.9882
		673	1.221	4.660	0.9816
n = 1.0	$r_o = -\frac{F_o}{m} \ln(1-x)$	648	0.424	1.618	0.9968
		658	1.111	4.240	0.9963
		673	1.830	6.985	0.9925
n = 1.5	$r_o = -\frac{F_o}{m} \frac{2}{(1-x)^{1/2}}$	648	0.441	1.683	0.9539
		658	1.226	4.679	0.9769
		673	2.147	8.195	0.9596
n = 2.0	$r_o = \frac{F_o}{m} \frac{x}{(1-x)}$	648	0.458	1.748	0.9524
		658	1.354	5.168	0.9714
		673	2.520	9.618	0.9479

<sup>a</sup> unit: ( $\text{mol s}^{-1} \text{g}_{\text{CAT}}^{-1}$ )

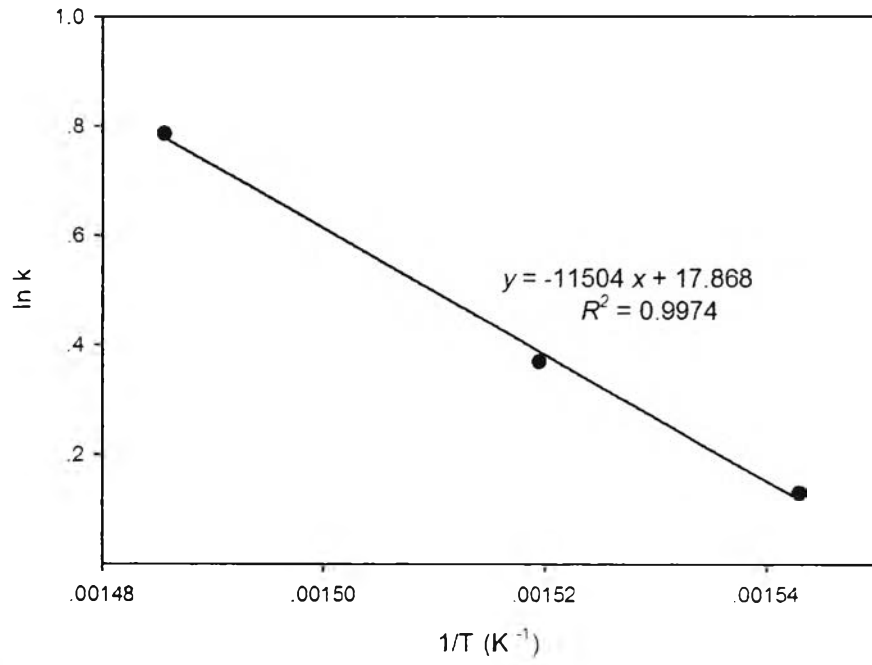
<sup>b</sup> unit: if n = 0, ( $\text{mol s}^{-1} \text{g}_{\text{CAT}}^{-1}$ ); if n = 1.0, ( $\text{l s}^{-1} \text{g}_{\text{CAT}}^{-1}$ ); if n = 1.5, ( $\text{mol}^{-0.5} \text{l}^{1.5} \text{s}^{-1} \text{g}_{\text{CAT}}^{-1}$ ),

and if n = 2.0, ( $\text{mol}^{-1} \text{l}^2 \text{s}^{-1} \text{g}_{\text{CAT}}^{-1}$ ).



**Figure 6.8** The reaction order determination by power-law kinetic model





**Figure 6.9** Arrhenius plot for the determination of kinetic parameters

## 6.5 Conclusion

In conclusion, ceria-zirconia mixed metal oxide catalysts were effective for the deoxygenation of oleic acid via direct decarboxylation resulting in the selective producing of C<sub>17</sub>-hydrocarbons and CO<sub>2</sub>. Among all catalysts, Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> catalyst was found to exhibit the highest catalytic activity relating to its highest reducibility. The kinetic of the deoxygenation reaction was found to perfectly fit with the first order kinetic model which confirms the direct decarboxylation mechanism, with the activation energy of ca. 23 kcal mol<sup>-1</sup>.

## 6.6 Acknowledgements

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