



## CHAPTER IV

### RESULTS AND DISCUSSION

Transesterification reaction of palm olein oil and coconut oil using heterogeneous calcium oxide (CaO) and magnesium oxide (MgO) base catalysts is investigated. The catalysts are fresh CaO, fresh MgO, modified CaO and modified MgO. Ammonium and potassium compound are used as modifying agents. All experiments of transesterification reaction are conducted at a temperature of 60°C, ambient pressure, a methanol to oil ratio of 6:1 and various concentrations of loading catalysts. The catalysts were separated from methyl esters phase and methyl esters was separated from methanol by evaporation. Methyl esters sample was analyzed for methyl esters content by gas chromatography. The analysis results are summarized in Tables D1. to D5. in Appendix D. Results and discussion are presented in eight parts:

- 4.1 Characterization of palm olein oil and coconut oil.
- 4.2 Characterization of catalysts.
- 4.3 Characterization of modified catalysts.
- 4.4 Effect of catalysts calcinations on yield of methyl esters
- 4.5 Effect of concentration of ammonium and potassium compounds on modified catalysts.
- 4.6 Effect of concentration of ammonium and potassium compounds of modified catalysts on yield of methyl esters.
- 4.7 Effect of type of oils on yield of methyl esters.
- 4.8 Life cycle of Catalysts.

#### 4.1 Characterization of palm olein oil and coconut oil.

Vegetable oils used in this research are commercial grade palm olein oil and coconut oil. Palm olein oil is clear yellow liquid at room temperature and coconut oil is clearer liquid than palm olein oil. The palm olein oil and coconut oil used in this study were characterized by measuring its properties. The measurement procedure and raw data are shown in Appendix A. The results are summarized in Table 4.1.

**Table 4.1** The properties of palm olein oil and coconut oil

Properties	Palm olein oil	Coconut oil
Free fatty acid, %	as palmitic acid	as lauric acid
	0.11	0.28
Acid value, mg KOH/g	0.47	0.70
Saponification value, mg KOH/g oil	210	247
Molecular weight, g/mole	801	681
Iodine value, g I <sub>2</sub> /100 g of oil	54	10

Table 4.1 shows the properties of palm olein oil and coconut oil. Free fatty acid value is a measure of free fatty acid concentration. The quantity of free fatty acids is an important parameter in production of methyl esters because free fatty acid value higher than 3% which cause soap formation. The results show that free fatty acids value of palm olein oil and coconut oil were 0.28 and 0.30 % respectively which palm olein oil and coconut oil indicted difficultly soap formation because free fatty acid value of both oil are lower than 3%. Meher et al. (2006) studied effect of free fatty acid on yield of methyl esters in transesterification reaction. The experiments carry out to titrated free fatty acid of vegetable oil by AOCS Official methods. The resultd found

that a free fatty acid (FFA) value lower than 3% is needed which effect to cause difficult soap formation.

Acid value or acid number is a measure of acid strength of oil. The acid value cause soap formation and European standard, (EN ISO 660) determined acid value less than 2.0 mg KOH/g of oil because acid value of oil higher than 2.0 mg KOH/g of oil which cause easy soap formation. The results show that acid value of palm olein oil and coconut oil are 0.47 mg-KOH/g and 0.70 mg-KOH/g respectively which indicate difficult soap formation due to acid value of both oil are lower than 2.0 mg KOH/g of oil.

Saponification value indicated ability of soap formation. Vegetable oils having high saponification value gives low yield of methyl esters. The average molecular weight of palm olein oil and coconut oil are calculated from saponification value as shown in Appendix A.

Iodine value is a measure of total unsaturation within fatty. European standard, (EN 14111) determined iodine value less than 120 g I<sub>2</sub>/100 g of oil. The iodine value content in palm olein oil is about 54 g I<sub>2</sub>/100 g of oil while the iodine value content in coconut oil is about 10 g I<sub>2</sub>/100 g of oil. Both oils have lower iodine value than European standard of oil.

**Table 4.2** Fatty acid composition in palm olein oil and coconut oil

Fatty acid	Structure <sup>a</sup>	Fatty acids composition, %wt.	
		Palm olein oil	Coconut oil
Caprylic	8:0	nd	0.66
Capric	10:0	nd	nd
Lauric	12:0	nd	48.85
Myristic	14:0	1.06	19.98
Palmitic	16:0	38.31	10.62
Palmitoleic	16:1	0.26	nd
Stearic	18:0	nd	3.20
Oleic	18:1	49.92	14.30
Linoleic	18:2	10.07	2.37
Linolenic	18:3	0.38	nd
Molecular weight, g/mole		813	680

<sup>a</sup>xx:y indicates x carbon in fatty acid chain with y double bonds.

nd = not detected

The fatty acid composition in palm olein oil and coconut oil are shown in Table 4.2. The major fatty acid components in palm olein oil are palmitic acid and oleic acid, while the major fatty acid components in coconut oil are lauric acid and myristic acid. The average molecular weight of palm olein oil and coconut oil is calculated from fatty acid composition as 813 and 680 g/mole respectively.

The results concluded that palm olein oil and coconut oil do not have different of free fatty acid, acid value and saponification value but palm olein oil has a higher iodine value than coconut oil because palm olein oil has more unsaturated fatty acid. Saponification value and fatty acid composition in oils are used to calculate molecular weight of oils. The both methods are nearly molecular weight value of oils.

## 4.2 Characterization of catalysts.

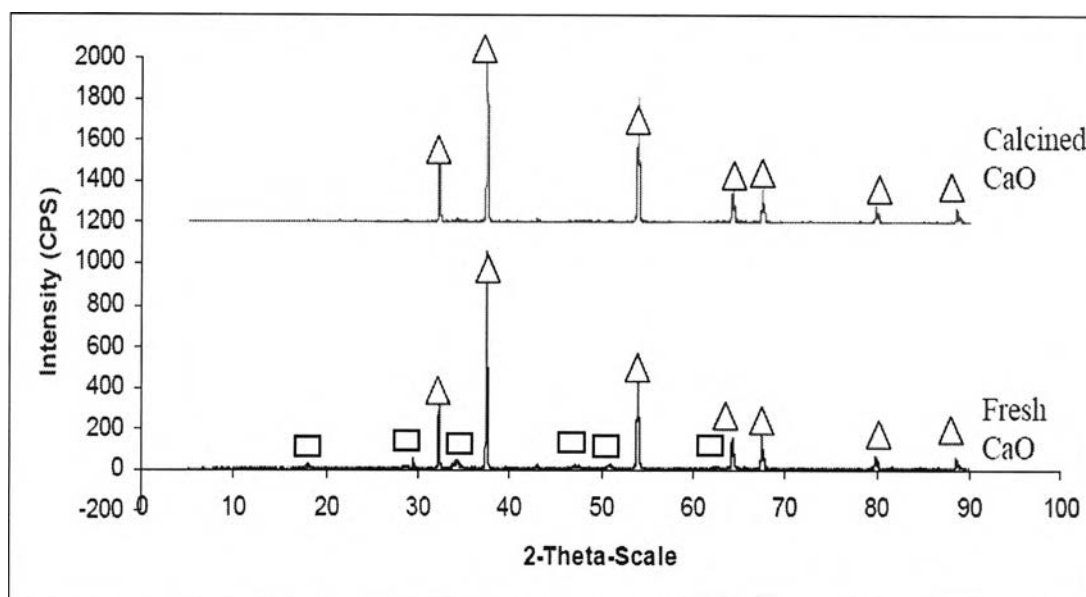
Fresh CaO, Fresh MgO, calcined CaO and calcined MgO are used as catalysts in this study. Fresh CaO and MgO were calcined in air at a temperature of 600°C for 3 h at ambient pressure. All catalysts were kept in a desiccator before using in experiment. The analyzed physical properties of CaO and MgO catalyst were surface area, pore volume and pore size of catalysts were the important factors for catalysts, which were determined by BET analysis. The results of CaO, MgO, calcined CaO and calcined MgO catalysts are shown in Table 4.3. XRD analyses of CaO, MgO, calcined CaO and calcined MgO catalysts were performed to obtain more information about the catalyst structures are shown in Figures 4.1 and 4.2.

**Table 4.3** Comparison of BET surface area, pore diameter and total pore volume various of catalysts.

Catalysts	Total Surface area (m <sup>2</sup> /g)	Average pore diameter (Å)	Average Pore volume (cc/g)
Fresh CaO	3	207.07	0.011
Calcined CaO	4.79	175.22	0.019
Fresh MgO	25.97	131.34	0.097
Calcined MgO	29.52	129.71	0.108

The results indicate that total surface area, average pore diameter and average pore volume of CaO and MgO increase after CaO and MgO are calcined at high temperature. XRD analysis shows the presence of Ca(OH)<sub>2</sub> peaks on fresh CaO catalyst and Ca(OH)<sub>2</sub> peaks disappeared after fresh CaO was calcined as shown in Figure 4.1. Nattamon et al. (2009) studied the structure of CaO catalysts before and after activation catalysts. The catalysts were calcined at temperature of 500°C for 10 h. The results indicate that

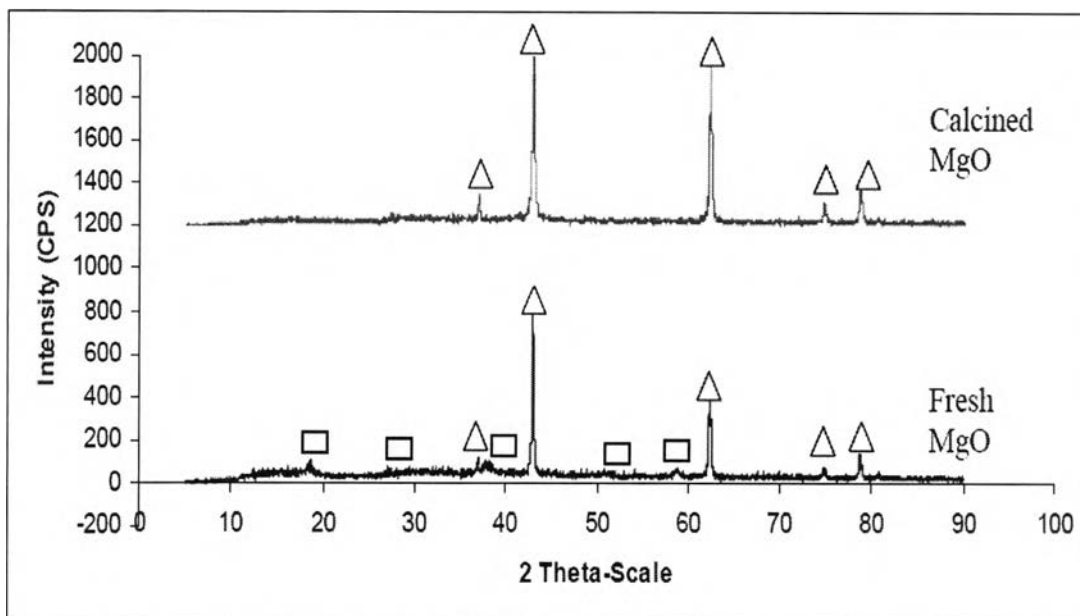
structure of CaO catalysts have clearly CaO peaks and showed Ca(OH)<sub>2</sub> on the fresh CaO.



**Figure 4.1** XRD patterns of fresh CaO and calcined CaO catalysts

(  $\square$  Ca(OH)<sub>2</sub>  $\triangle$  CaO )

XRD analysis in Figure 4.2 shows the presence of Mg(OH)<sub>2</sub> peaks on fresh MgO catalyst but Mg(OH)<sub>2</sub> peaks disappeared after MgO was calcined. Selahattin et al. (1999) studied the structure of MgO catalysts before and after activated by calcined at 500<sup>0</sup>C for 6 h. XRD results shown uncalcined MgO showed the peak of MgO and Mg(OH)<sub>2</sub>. After calcination MgO catalysts with air at high temperature Mg(OH)<sub>2</sub> peak disappeared which indicated Mg(OH)<sub>2</sub> was removed from surface of MgO catalyst.



**Figure 4.2** XRD patterns of fresh MgO and calcined MgO catalysts  
( □ Mg(OH)<sub>2</sub>   Δ MgO )

Fresh CaO is partially transformed to Ca(OH)<sub>2</sub> by moisture in air as shown in equation (4.1). This mechanism of formation of Ca(OH)<sub>2</sub> on CaO catalyst is similarly with Mg(OH)<sub>2</sub> formation on fresh MgO as shown in equation (4.2) when they were stored.



Absorbed water on both catalysts cause Ca(OH)<sub>2</sub> and Mg(OH)<sub>2</sub> formation respectively and cover an inner core of CaO and MgO result to reduce surface area. Claire et al. (2008) studied the transesterification reaction of rapeseed oil to biodiesel. The experiments used 2 %wt of reused CaO, which catalysts were calcined at temperature of 600°C for 5 h. The results concluded that CaO catalyst performance and stability were reduced by moisture in air. Surface area was improved by an increase of calcinations

temperature. The catalysts were calcined at temperature of 600°C for 5 h. Calcination of treated CaO catalysts at high temperatures resulted in removing of CaCO<sub>3</sub> and Ca(OH)<sub>2</sub>.

However, equations (4.1) and (4.2) are reversible reaction. The formation of Ca(OH)<sub>2</sub> from CaO with moisture and Mg(OH)<sub>2</sub> from MgO with moisture respectively. Calcinations both fresh CaO and MgO at high temperature reverses Ca(OH)<sub>2</sub> to CaO and Mg(OH)<sub>2</sub> to MgO. So calcinations of CaO and MgO catalyst eliminate Ca(OH)<sub>2</sub> and Mg(OH)<sub>2</sub> which result to increase surface area and pore volume of both catalysts. Kouzu et al. (2008) studied calcium oxide as a solid base catalyst for transesterification reaction of soybean oil. The experiments used 1 %wt of reused CaO, CaCO<sub>3</sub> and Ca(OH)<sub>2</sub> which catalysts were calcined at temperature of 900°C for 1.5 h. The results concluded that calcined CaO had larger pore size than CaO because calcinations at high temperature eliminated the contaminant in the pore. Granados et al. (2007) studied the activity of activated CaO as a catalyst in the production of biodiesel by transesterification reaction of triglycerides with methanol. The experiments used 2 %wt of reused CaO which the catalysts were calcined at temperature of 600°C for 2 h. The results concluded that Ca(OH)<sub>2</sub> on surface of CaO catalysts was not active as the catalyst in transesterification reaction of sunflower oil so decarbonation of CaO catalysts was important. It was found that calcination at 600°C was able to remove Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> completely and the calcined catalyst were high activity and gave yield of methyl esters content of 90 %. Monica et al. (2008) studied the transesterification reaction activity of sunflower oil to biodiesel. The experiments used 1 %wt of CaO and MgO which the catalysts were calcined at temperature of 800°C for 1 h. The results concluded that the surface area was improved by increasing of calcinations temperature. The catalysts were calcined at temperature of 800°C for 1 h. Calcination of treated MgO at high temperatures resulted in the eliminating Mg(OH)<sub>2</sub>.



The results found that calcinations at 600°C for 3 h was able to remove  $\text{Ca}(\text{OH})_2$  on the CaO catalyst and remove  $\text{Mg}(\text{OH})_2$  on the MgO catalyst. It summarize the CaO and MgO must be calcined before using for experiment and kept in condition without moisture.

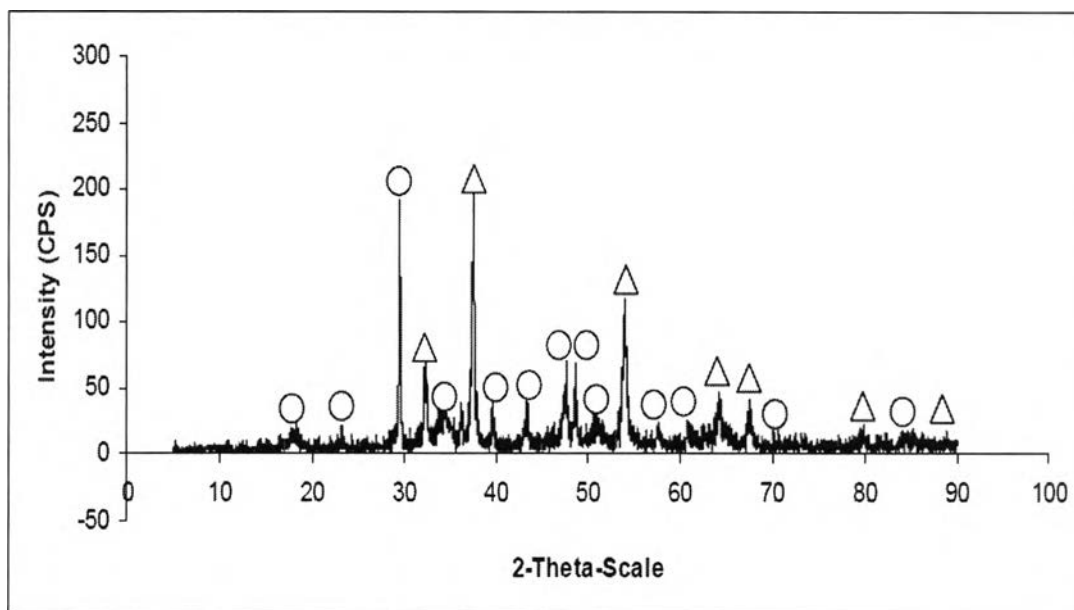
### 4.3 Characterization of modified catalysts.

Calcined  $(\text{NH}_4)_2\text{CO}_3/\text{CaO}$ ,  $\text{K}_2\text{CO}_3/\text{CaO}$ ,  $(\text{NH}_4)_2\text{CO}_3/\text{MgO}$  and  $\text{K}_2\text{CO}_3/\text{MgO}$  are used as catalysts in this study. CaO and MgO were also dipped into  $(\text{NH}_4)_2\text{CO}_3$  solution and  $\text{K}_2\text{CO}_3$  solution for 30 minutes. Solid parts were separated from the solution, dried in an oven at 110°C for 24 h and calcined at 600°C for 3 h. All catalysts were kept in a desiccator. The analyzed physical properties of modified catalysts by  $\text{K}_2\text{CO}_3$  and  $(\text{NH}_4)_2\text{CO}_3$  contained surface area, pore diameter and pore volume of modified catalysts were determined by BET analysis as shown in Table 4.4. XRD analyses of modified CaO and MgO catalysts were performed to obtain more information about the catalyst structures are shown in Figures 4.3 to 4.6.

**Table 4.4** Comparison of BET surface area, pore diameter and total pore volume in type of modified catalysts.

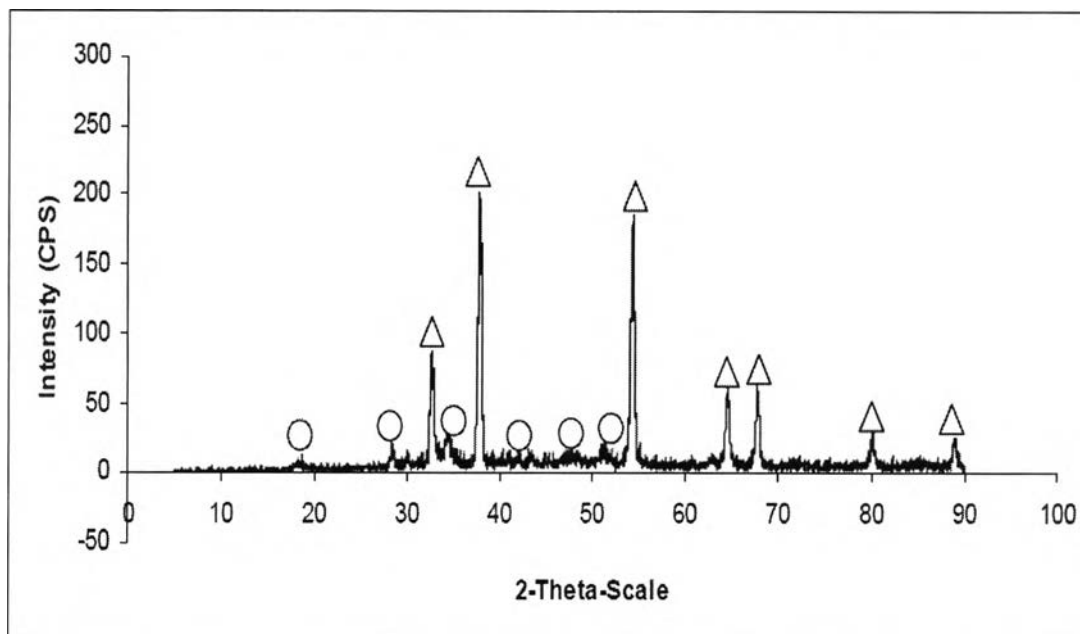
Catalysts	Modifying amount	Total Surface area ( $\text{m}^2/\text{g}$ )	Average pore diameter ( $\text{Å}$ )	Average Pore volume ( $\text{cc/g}$ )
Calcined CaO	-	4.79	175.22	0.019
$(\text{NH}_4)_2\text{CO}_3/\text{CaO}$	20%	18.71	129.66	0.056
$\text{K}_2\text{CO}_3/\text{CaO}$	20%	8.23	163.61	0.039
Calcined MgO	-	29.52	129.71	0.108
$(\text{NH}_4)_2\text{CO}_3/\text{MgO}$	20%	89.96	146.06	0.393
$\text{K}_2\text{CO}_3/\text{MgO}$	20%	31.05	151.59	0.151

Table 4.4 shows CaO and MgO modified by  $(\text{NH}_4)_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  are obtained higher surface area than unmodified CaO and MgO because CaO and MgO are well segregated crystals. The measured pore volume and pore size are space between crystal of modified substance and crystal of CaO and MgO so the loaded  $(\text{NH}_4)_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  on surface of catalysts could possibly be coated evenly on the outside surfaces of crystals. Maythinee et al (2007) studied biodiesel production from crude palm oil using  $\text{K}_2\text{CO}_3/\text{CaO}$  as heterogeneous catalyst. The catalysts were prepared by incipient wetness impregnation technique. The  $\text{K}_2\text{CO}_3$  dropped onto the CaO. After impregnations the catalysts were dried in oven at  $120^\circ\text{C}$  for 12 h following by calcination in air for 5 h at  $500^\circ\text{C}$ . The results concluded that CaO the crystals were well segregated and therefore the loaded  $\text{K}_2\text{CO}_3$  could possibly be coated evenly on the outside surfaces of crystals. This could probably explain the increase in BET surface area from 5.0 to  $7.3 \text{ m}^2/\text{g}$ . Nathamon et al (2006) studied biodiesel production from palm stearin using heterogeneous catalysts. The experiment carry out  $\text{NH}_4(\text{NO}_3)$  dropped onto the CaO. After impregnations the catalysts were dried in oven at  $120^\circ\text{C}$  for 12 h following by calcination in air for 10 h at  $550^\circ\text{C}$ . After calcination the catalysts were kept under a dehumidified condition. The results concluded that the loaded 15 %wt  $\text{NH}_4(\text{NO}_3)$  on CaO could possibly be coated evenly on the outside surfaces of crystals. This could probably explain the increase in BET surface area from 5.02 to  $7.06 \text{ m}^2/\text{g}$ . Mathew et al. (2006) studied about loaded Mo into CaO and MgO. The experiment carry out  $\text{NH}_4(\text{NO}_3)$  dropped onto the CaO. After impregnations the catalysts were dried in oven at  $120^\circ\text{C}$  for 12 h following by calcination in air for 5 h at  $550^\circ\text{C}$ . The results found that BET surface area of CaO increased from  $8 \text{ m}^2/\text{g}$  to  $16 \text{ m}^2/\text{g}$  and MgO increased from  $43 \text{ m}^2/\text{g}$  to  $136 \text{ m}^2/\text{g}$ . These catalysts have no pore because they have no porous structure. Pore size and pore volume resulted from BET analysis belonged to the voidages between crystals.



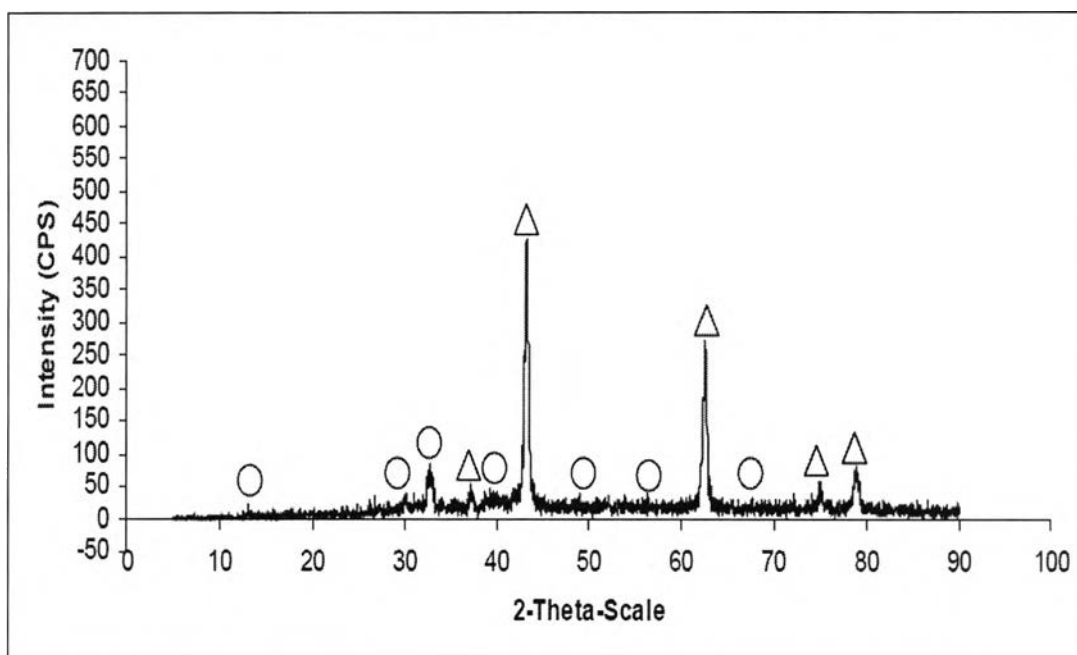
**Figure 4.3** XRD patterns of  $(\text{NH}_4)_2\text{CO}_3/\text{CaO}$  calcined at  $600^\circ\text{C}$

( ○  $(\text{NH}_4)_2\text{CO}_3/\text{CaO}$  △ CaO)



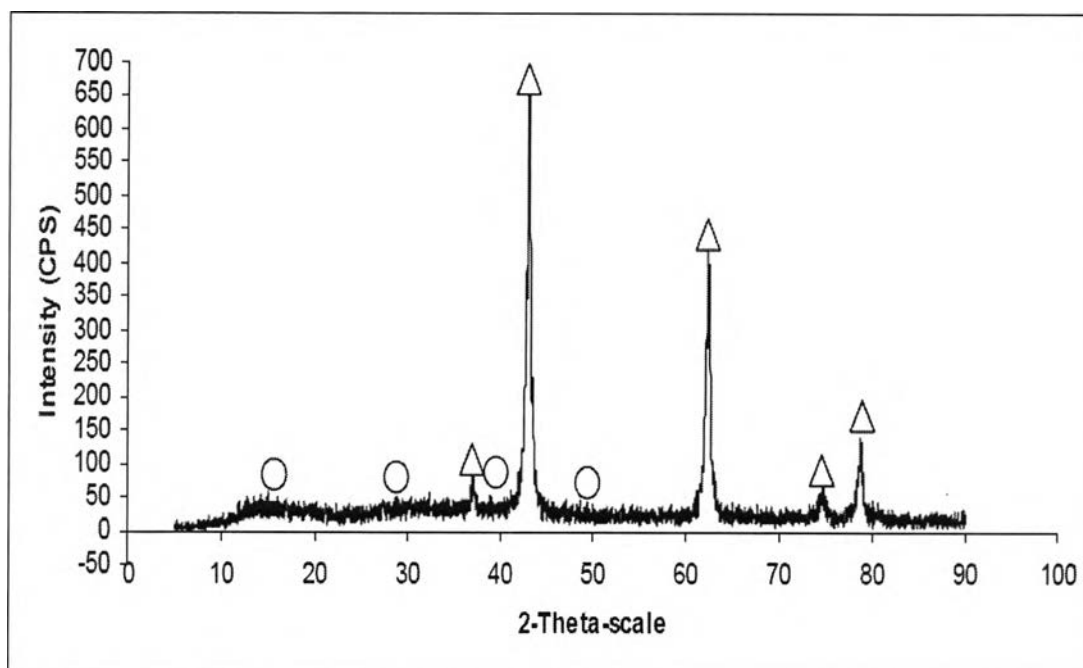
**Figure 4.4** XRD patterns of  $\text{K}_2\text{CO}_3/\text{CaO}$  calcined at  $600^\circ\text{C}$

( ○  $\text{K}_2\text{CO}_3/\text{CaO}$  △ CaO)



**Figure 4.5** XRD patterns of  $K_2CO_3/MgO$  calcined at  $600^\circ C$

( ○  $K_2CO_3/MgO$  △  $MgO$ )



**Figure 4.6** XRD patterns of  $(NH_4)_2CO_3/MgO$  calcined at  $600^\circ C$

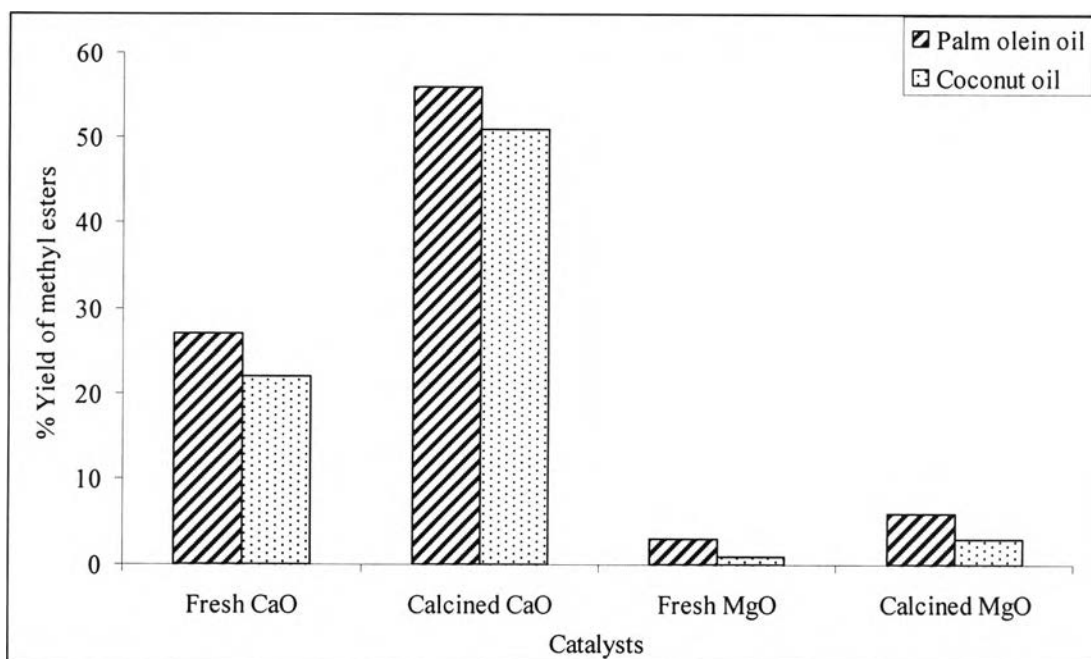
( ○  $(NH_4)_2CO_3/MgO$  △  $MgO$ )

Figures 4.3 to 4.6 show that XRD analysis result indicates  $(\text{NH}_4)_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  dispersed on structure of MgO. The XRD analysis showed  $(\text{NH}_4)_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  peaks were small but MgO peak was large.

The results conclude the surface area of modified catalysts with  $(\text{NH}_4)_2\text{CO}_3$  are higher than unmodified catalysts because  $(\text{NH}_4)_2\text{CO}_3$  could possibly be coated on the surface area. The modified catalysts with  $\text{K}_2\text{CO}_3$  gives similarly the result and reason of modified catalysts with  $(\text{NH}_4)_2\text{CO}_3$ .

#### 4.4 Effect of catalysts calcinations on yield of methyl esters

The effect of yield of methyl esters using fresh CaO, MgO, calcined CaO and calcined MgO are shown in Figure 4.7. The experiments were used 5 %wt of reused catalysts, molar ratio of methanol to oil of 6:1, reaction temperature of  $60^\circ\text{C}$ , reaction time of 2 h. and using THF as co-solvent .



**Figure 4.7** The effect of calcinations of different catalysts to yield of methyl esters using 5 %wt of reused catalysts, molar ratio of methanol to oil of 6:1, reaction temperature of  $60^\circ\text{C}$ , reaction time of 2 h and using THF as co-solvent.

Figure 4.7 shows calcined CaO obtained highest yield of transesterification reaction from both of palm olein oil and coconut oil about 56% and 50% respectively because the present of  $\text{Ca(OH)}_2$  on fresh CaO catalyst surface possibly obtain low yield. The results show that calcined CaO catalyst gives higher yield of methyl esters for both types of oils. The analysis results are summarized in Tables D2. and D3. in Appendix D. Masato et al. (2003) studied the synthesis of methyl esters using  $\text{CaCO}_3$ ,  $\text{Ca(OH)}_2$  and CaO catalysts. The experiment carry out with methanol to waste cooking oil ratio of 42:1, used 1 %wt of catalysts, calcinations CaO catalysts of  $900^\circ\text{C}$  for 1.5 h, reaction temperature of  $65^\circ\text{C}$  and reaction time of 4 h. The results showed that the catalytic activity was in the sequence of  $\text{CaO} > \text{Ca(OH)}_2 > \text{CaCO}_3$  and gave the yield of Fatty acid methyl esters was 93% for CaO, 12% for  $\text{Ca(OH)}_2$  and 0% for  $\text{CaCO}_3$  under the same reacting condition in 1 h of reaction time. The  $\text{Ca(OH)}_2$  and  $\text{CaCO}_3$  did not active and gave lower yield of methyl esters because the crystallization of  $\text{Ca(OH)}_2$  and  $\text{CaCO}_3$  on surface area of CaO had low activity.

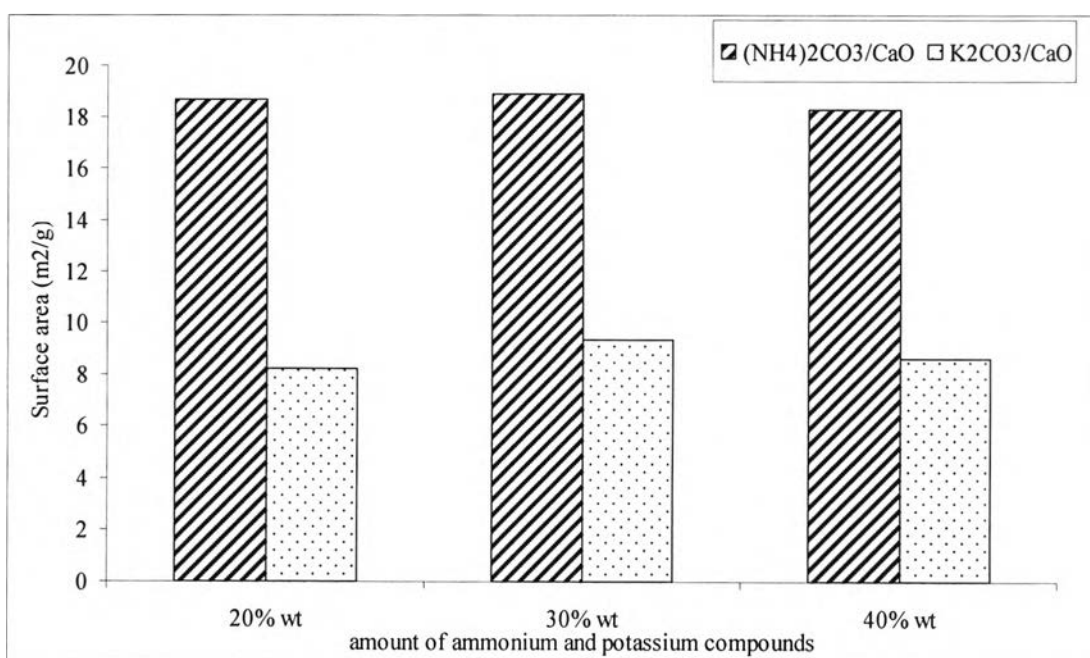
The fresh MgO and calcined MgO obtain lower yield of methyl esters than fresh and calcined CaO because both fresh and calcined MgO are low active although the fresh and calcined MgO have a high surface area. Gryglewicz (2000) studied the transesterification reaction of rapeseed oil. The experiment carry out with methanol to rapeseed oil ratio of 45:1, used 5 %wt of reused calcium oxide and magnesium oxide, reaction temperature of  $65^\circ\text{C}$  and reaction time of 2 h. The results concluded that it was low or no activity using MgO in transesterification reaction performed at boiling point of methanol due to its weak basic property. Arzamendi et al. (2008) studied the catalytic activity and selectivity of several compounds of the  $\text{K}_2\text{CO}_3$ , CaO and MgO catalyst in the transesterification reaction. The experiment carry out with methanol to refined sunflower oil ratio of 12:1, reaction temperature of  $65^\circ\text{C}$ , molar methanol to oil ratio of 12:1 and reaction time of 1.30 h. The results

concluded that fresh and calcined MgO were also poorly active in spite of their relatively high specific areas. Masato et al. (2008) studied the transesterification reaction using alkaline-earth metal oxides of soybean oil. The experiment carry out with methanol to waste cooking oil ratio of 42:1, used 1 %wt of catalysts, calcinations CaO catalysts of 900°C for 1.5 h, reaction temperature of 65°C and reaction time of 4 h. The results showed that the sequence of SrO > CaO > MgO and the basic strength was in sequence of SrO > CaO > MgO because the basic properties seemed to be determinant for the catalytic activity. Vicente et al. (1998) studied the reaction of refined sunflower oil and methanol was carried out over fresh and calcined MgO catalysts. The experiment carry out with methanol to refined sunflower oil ratio of 6:1, used 1 %wt of reused magnesium oxide reaction temperature of 60°C and reaction time of 8 h. The results concluded that the yield was 11% conversion of MgO from transesterification of refined sunflower oil. It was confirmed in this study that MgO has low performance.

The results conclude that calcined CaO at high temperature obtain higher yield of methyl esters than calcined MgO, which used in tranesterification from palm olein oil and coconut oil because MgO catalyst has low active or not active in tranesterification reaction. Although MgO catalyst higher surface area than CaO catalyst. The yield of methyl esters for the transesterification reaction over the different catalysts are in the following order: calcined CaO > fresh CaO > calcined MgO > fresh MgO.

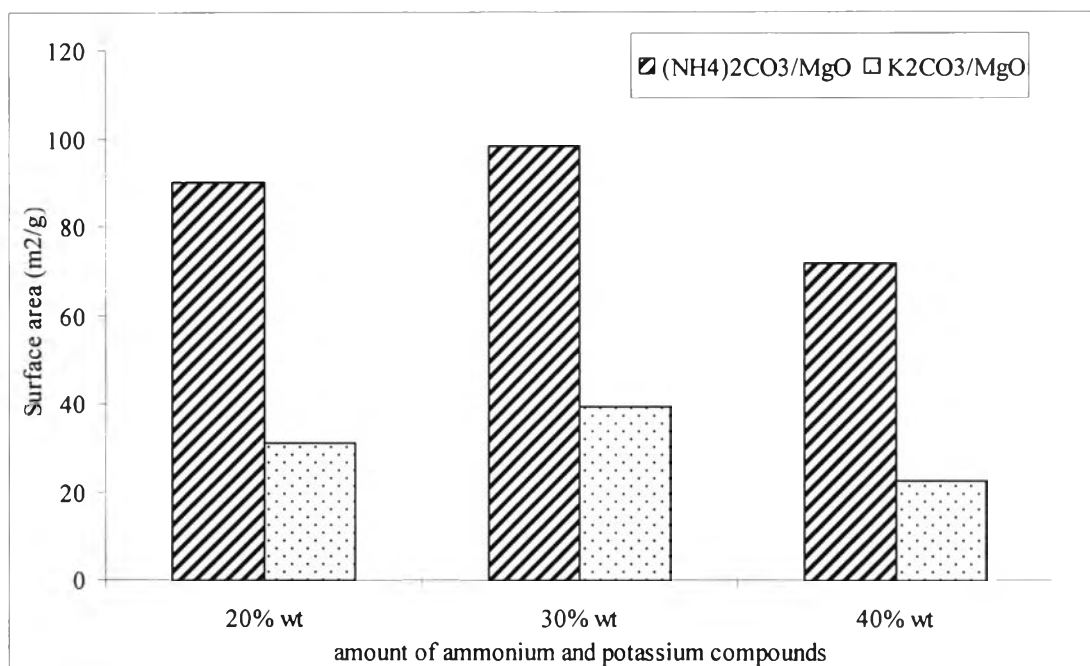
#### 4.5 Effect of concentration of ammonium and potassium compounds on modified catalysts.

The comparison of concentration of  $(\text{NH}_4)_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  on surface area pore diameter and pore volume of CaO and MgO catalysts were analyzed by BET. The results of analyzing BET are shown in Figures 4.8 and 4.9.



**Figure 4.8** The effect of concentration of ammonium and potassium compounds modified CaO catalysts.





**Figure 4.9** The effect of amount of ammonium and potassium compounds modified MgO catalysts.

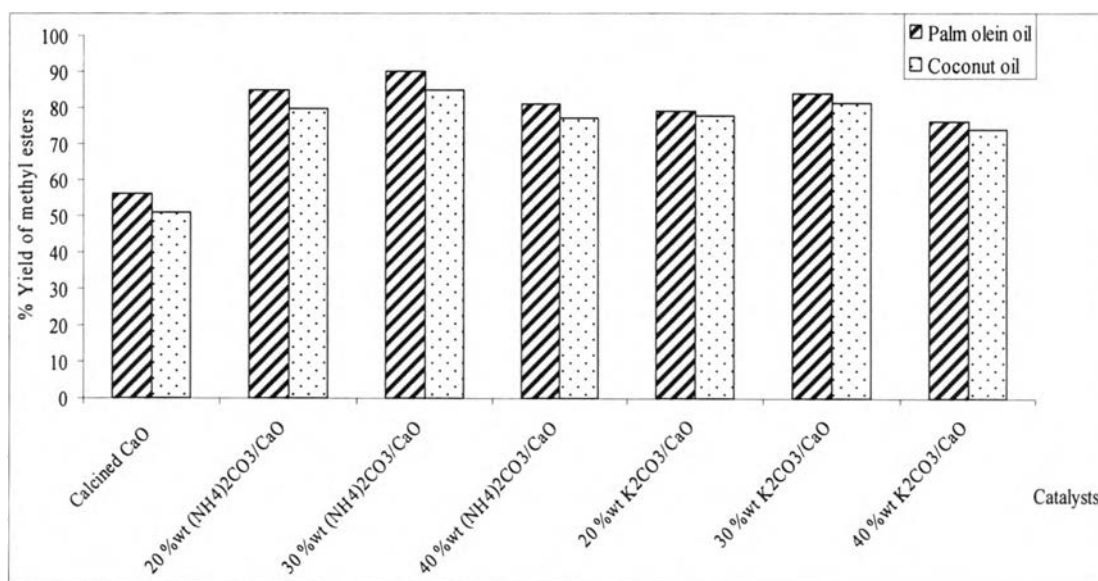
Figures 4.8 and 4.9 show effect of concentration of loaded (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>/CaO, K<sub>2</sub>CO<sub>3</sub>/CaO, (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>/MgO and K<sub>2</sub>CO<sub>3</sub>/MgO catalyst on surface area. The results indicate increasing concentration of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> on CaO catalyst to 30% wt, surface area trend of these catalysts increase, the highest surface area of these catalysts were 18.86 m<sup>2</sup>/g for (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>/CaO and 9.36 m<sup>2</sup>/g for K<sub>2</sub>CO<sub>3</sub>/CaO the analysis results are summarized in Table 1. in Appendix D. However, when increasing concentration of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> on CaO catalyst is over 30%, surface area trend of these catalyst decrease because excessive concentration of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> could agglomerate on the surface of catalysts. According to Figure 4.9 shows effect of concentration of loaded (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> on MgO was increased to 30 %wt, the highest surface area of these catalysts are 98 m<sup>2</sup>/g for (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>/ MgO and 30 m<sup>2</sup>/g for K<sub>2</sub>CO<sub>3</sub>/ MgO the analysis results are summarized in Table 1. in Appendix D. However, the loading concentration of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> on MgO catalysts are over

30 %wt, the yield of methyl esters decrease. These result has similar trend with loaded  $(\text{NH}_4)_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  on CaO. Xie et al (2006) studied the effect of the loading amount of  $\text{KNO}_3$  on the conversion of soybean oil at the loading amount range 15 to 45 %wt. The experiment carry out with methanol to soybean oil ratio of 15:1, a catalyst amount 6.5%, temperature of  $70^\circ\text{C}$ , reaction time of 7 h. and calcinated at  $500^\circ\text{C}$  for 5 h. The results showed that the catalyst with 35 %wt  $\text{KNO}_3$  loaded on  $\text{Al}_2\text{O}_3$  gave the highest surface area. However, when the loaded  $\text{KNO}_3$  was over 35 %wt, the surface area decreased because the excess  $\text{KNO}_3$  covered the surface basic site.

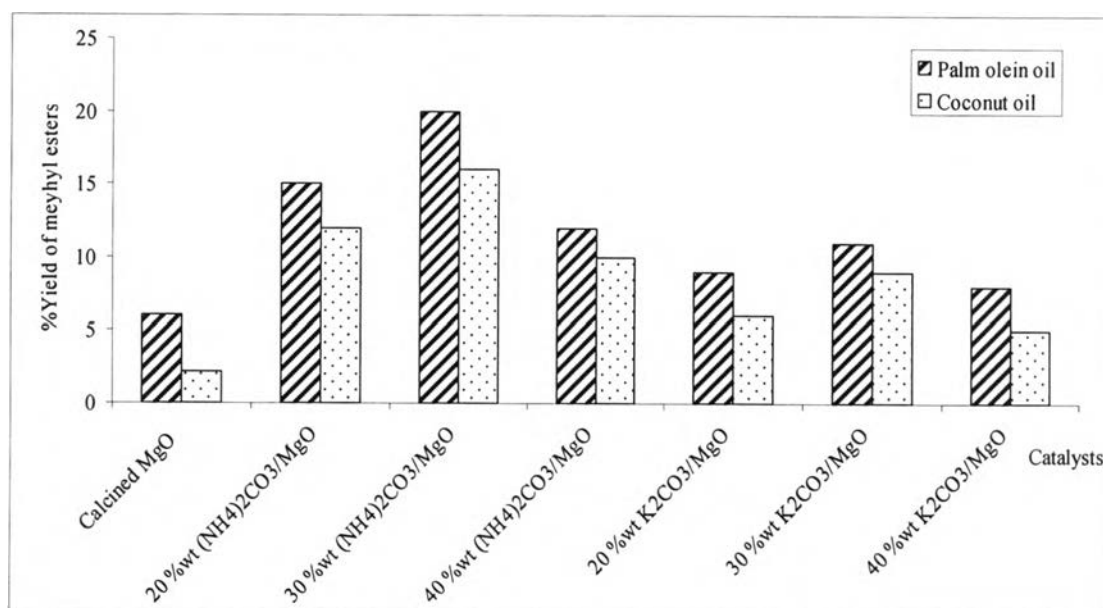
The results conclude that concentration of  $(\text{NH}_4)_2\text{CO}_3$  are 30 %wt, which gives the highest surface area of CaO catalyst because there are proper amount of  $(\text{NH}_4)_2\text{CO}_3$  cover the surface of catalyst.

#### **4.6 Effect of concentration of ammonium and potassium compounds of modified catalysts on yield of methyl esters.**

In order to study the effect of concentration of loaded  $\text{K}_2\text{CO}_3$  and  $(\text{NH}_4)_2\text{CO}_3$  on CaO and MgO catalyst on catalytic activities,  $\text{K}_2\text{CO}_3/\text{CaO}$ ,  $(\text{NH}_4)_2\text{CO}_3/\text{CaO}$ ,  $\text{K}_2\text{CO}_3/\text{MgO}$  and  $(\text{NH}_4)_2\text{CO}_3/\text{MgO}$  sample with the loading amount of  $\text{K}_2\text{CO}_3$  and  $(\text{NH}_4)_2\text{CO}_3$  ranging from 20 to 40 %wt, were prepared and catalyzed transesterification reaction. The results are shown in Figures 4.10 and 4.11.



**Figure 4.10** The effect of loading  $(\text{NH}_4)_2\text{CO}_3/\text{CaO}$  and  $\text{K}_2\text{CO}_3/\text{CaO}$  on yield of methyl esters using 5 %wt of reused catalysts, molar ratio of methanol to oil of 6:1, reaction temperature of  $60^\circ\text{C}$ , reaction time of 2 h and using THF as co-solvent.



**Figure 4.11** The effect of  $(\text{NH}_4)_2\text{CO}_3/\text{MgO}$  and  $\text{K}_2\text{CO}_3/\text{MgO}$  on yield of methyl esters using 5 %wt of reused catalysts, molar ratio of methanol to oil of 6:1, reaction temperature of  $60^\circ\text{C}$ , reaction time of 2 h and using THF as co-solvent.

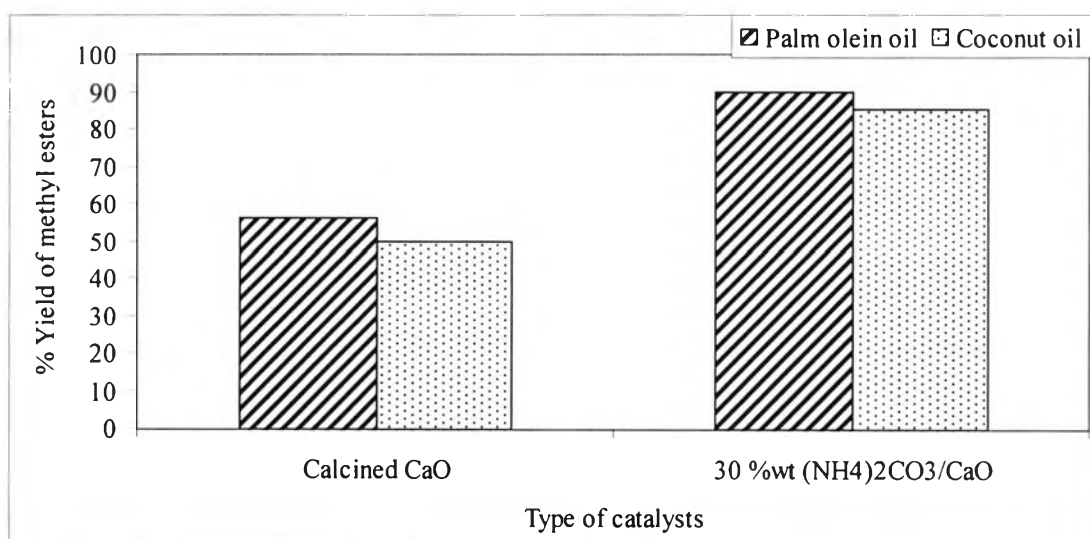
Figures 4.10 and 4.11 show effect of concentration of loaded  $(\text{NH}_4)_2\text{CO}_3/\text{CaO}$ ,  $\text{K}_2\text{CO}_3/\text{CaO}$ ,  $(\text{NH}_4)_2\text{CO}_3/\text{MgO}$  and  $\text{K}_2\text{CO}_3/\text{MgO}$  catalyst on yield of methyl ester, when concentration of loaded  $(\text{NH}_4)_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  on CaO increased to 30 %wt, yield of methyl esters of palm olein oil and coconut oil increased, and highest yield of methyl esters using  $(\text{NH}_4)_2\text{CO}_3$  on CaO catalyst are 90% for palm olein oil, 85% for coconut oil and highest yield of methyl esters using  $\text{K}_2\text{CO}_3$  on CaO catalyst were 84% for palm olein oil, 81% for coconut oil. The analysis results were summarized in Tables D2. to D3 in Appendix D. However when loaded amount of loaded  $(\text{NH}_4)_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  on CaO are over 30 %wt, yield of methyl esters of same catalyst and oil is decreased because excessive concentration of  $(\text{NH}_4)_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  could cover the active site on the catalyst surface and cause to decrease catalytic activity. According to Figure 4.11 shows effect of concentration of loaded  $(\text{NH}_4)_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  on MgO increase to 30 %wt, which obtain highest yield of methyl esters of both oil. However, the loading concentration of  $(\text{NH}_4)_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  on MgO catalysts are over 30 %wt, the yield of methyl esters were decreased. These result has similar trend with loaded  $(\text{NH}_4)_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  on CaO. Huaping et al (2006) studied preparation of biodiesel catalyzed by solid super base of calcium oxide. The experiment carry out with methanol to jatropha curcas oil ratio of 9:1, used 1.5 %wt of reused calcium oxide reaction temperature of  $70^\circ\text{C}$ , reaction time of 2.5 h. and dipped CaO into a 0.12 g/ml ammonium carbonate solution. The results showed that the base strength of CaO had more than 26.5 after modified CaO with ammonium carbonate solution gave the highest conversion of 93% for jatropha curcas oil. Maythinee et al. (2007) studied biodiesel production from crude palm oil using  $\text{K}_2\text{CO}_3/\text{CaO}$  as heterogeneous catalyst. The experiment carried out with methanol to refined sunflower oil ratio of 26:1, used 6 %wt of reused calcium oxide reaction temperature of  $60^\circ\text{C}$ , 20 wt% THF, 300 rpm stirring speed, reaction time of 3 h and 5 to 35 %wt of  $\text{K}_2\text{CO}_3/\text{CaO}$  catalysts.

The result show increasing the loading amount of  $K_2CO_3$  affect to increase the yield of methyl esters because the  $K_2CO_3$  is active site on CaO but increasing the loading amount of  $K_2CO_3$  is over 35 %wt that does not increase yield of methyl esters due to the agglomeration of catalyst and coverage of surface basic sites by the excessive  $K_2CO_3$ . Xie et al. (2006) studied the effect of KI loading on  $Al_2O_3$  and they found that at the loading of 35 %wt of KI on  $Al_2O_3$  exhibited the highest conversion of 84.7% for soybean oil. Boonsirm Prasomsan and Apinya Daungchan (2007) studied transesterification reaction of palm olein oil to biodiesel using amounts of  $Ca(NO_3)_2$  from 30, 38 and 50%wt as a heterogeneous catalysts. The experiment carry out with methanol to palm olein oil ratio of 30:1, a catalyst amount 1%, temperature of 60°C, reaction time of 1 h. The results showed that there was an electronic effect between  $Ca(NO_3)_2$  loading and CaO support according to the reaction between  $Ca^{2+}$  and CaO. The 38 %wt  $Ca(NO_3)_2$ /CaO provided the maximum yield compared with 30 %wt  $Ca(NO_3)_2$ /CaO and 50 %wt  $Ca(NO_3)_2$ /CaO because lower amount of  $Ca(NO_3)_2$  loading decreased active sites and the higher amount caused the coverage of excess  $Ca(NO_3)_2$ , which is responsible for the decrease in conversion.

The results conclude that the catalytic activity of catalysts are in the following order:  $NH_4(CO_3)_2$ /CaO >  $K_2CO_3$  /CaO > calcined CaO and  $NH_4(CO_3)_2$ /MgO >  $K_2CO_3$  /MgO > calcined MgO because the surface area of  $NH_4(CO_3)_2$ /CaO is higher than the other catalysts. Moreover,  $NH_4(CO_3)_2$ /CaO shows the highest catalytic activity and obtained the highest methyl esters content.

#### 4.7 Effect of type of oils on yield of methyl esters.

In order to study and compare tranesterification of palm olein oil and coconut oil used 5 %wt of reused calcined CaO and  $\text{NH}_4(\text{CO}_3)_2/\text{CaO}$ , molar ratio of methanol to oil of 6:1, reaction temperature of  $60^\circ\text{C}$ , reaction time of 2 h. and using THF as co-solvent. The results are shown in Figure 4.12.



**Figure 4.12** Type of oils on yield of methyl esters using 5 %wt of reused catalysts, molar ratio of methanol to oil of 6:1, reaction temperature of  $60^\circ\text{C}$ , reaction time of 2 h and using THF as co-solvent.

Figure 4.12 shows effect of palm olein oil and coconut oil on tranesterification. The same type of catalysts provided yield of methyl esters from palm olein oil is almost high with yield of methyl esters from coconut oil because physical properties and fatty acid compositions of both oil are almost similar and almost obtain yield of methyl esters. The analysis results are summarized in Tables D2. and D3 in Appendix D. Sita et al. (2008) studied tranesterification reaction of palm kernel oil and coconut oil with using methanol and heterogeneous catalysis as  $\text{Al}_2\text{O}_3$  supported alkali and alkali earth metal oxides. The experiment carry out with methanol to oil ratio of 65:1, used

20% (w/w) catalyst to oil ratio for PKO and CCO, reaction temperature of 60°C and reaction time of 3 h. The results showed that yield of methyl esters from coconut oil was lower than yield of methyl esters from palm kernel oil. It could be concluded the higher free fatty acid (acid value) in coconut oil which results in a deactivation of some basic sites of the catalyst through the base neutralization. Jaturong et al. (2008) studied type of oil. The yield of methyl esters was 90.3% for crude palm kernel oil and 86.3 %wt for crude coconut oil under the same conditions. The methyl esters produced from crude palm kernel oil was higher than crude coconut oil because coconut oil probably had the higher amount of free fatty acid and water content than the crude palm kernel oil, which effected to a deactivation of some basic sites of the catalyst

The results conclude that the transesterification reaction of palm olein oil and coconut oil at same condition found both oil give similar yield of methyl esters because physical properties and fatty acid compositions of both oil were almost similar and almost obtain yield of methyl esters.

#### **4.8 Life cycle of Catalyst.**

Heterogeneous catalysts have the potential to be recovered, regenerated and reused. This section investigated and compared activity of catalysts after repeatedly used. The reused catalysts were separated the catalyst from product was washed by methanol, which will be used in the next experiment. Study of deactivated catalysts were carried out with CaO and MgO modified with 30 %wt of  $(\text{NH}_4)_2\text{CO}_3$  as shown in Tables 4.5.

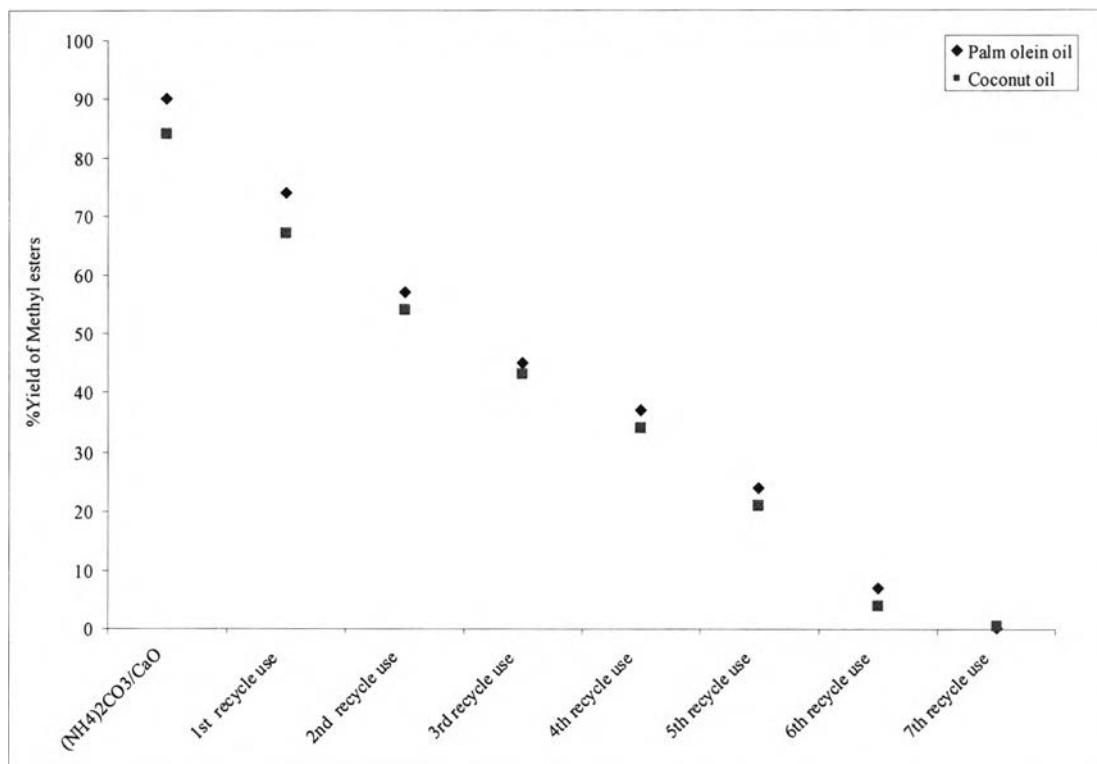
**Table 4.5** Life cycle of catalyst on yield of methyl esters.

Catalysts	Total Surface area (m <sup>2</sup> /g)	%Yield of Methyl esters	
		Palm olein oil	Coconut oil
(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> /CaO	18.86	90	85
1 <sup>st</sup> recycle use	11.44	74	68
2 <sup>nd</sup> recycle use	7.45	57	54
3 <sup>rd</sup> recycle use	3.14	46	44
4 <sup>th</sup> recycle use	2.19	39	35
5 <sup>th</sup> recycle use	1.33	24	22
6 <sup>th</sup> recycle use	1.27	8	4
7 <sup>th</sup> recycle use	0.88	0.2	0.5
(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> /MgO	98.08	20	16
1 <sup>st</sup> recycle use	37.42	9	7
2 <sup>nd</sup> recycle use	21.96	4	3
3 <sup>rd</sup> recycle use	10.86	2	0.8
4 <sup>th</sup> recycle use	8.72	0.3	0.1

The results in Table 4.5 indicate that the activity of 30 %wt of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>/CaO and 30 %wt of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>/MgO catalysts, which obtain highest yield of methyl esters and surface area. However, when use repeated catalyst in experiments, yield of methyl esters rapidly decrease. These results correspond that surface area of catalysts decreases as showed in Table 4.5. The activity of catalyst decrease which result from dissolve ammonium compound in the methanol because methanol removes the active sites of the catalyst. Liu et al. (2008) studied the reusability of K<sub>2</sub>CO<sub>3</sub>/CaO. The experiment carry out with methanol to oil ratio of 12:1, used 8% (w/w) catalyst to oil ratio for soybean oil, reaction temperature of 70°C and reaction time of 1.5 h. The results indicated that the activity of K<sub>2</sub>CO<sub>3</sub>/CaO rapidly decreases during the repeated experiments, the biodiesel yields decreased from 81% to 81% after



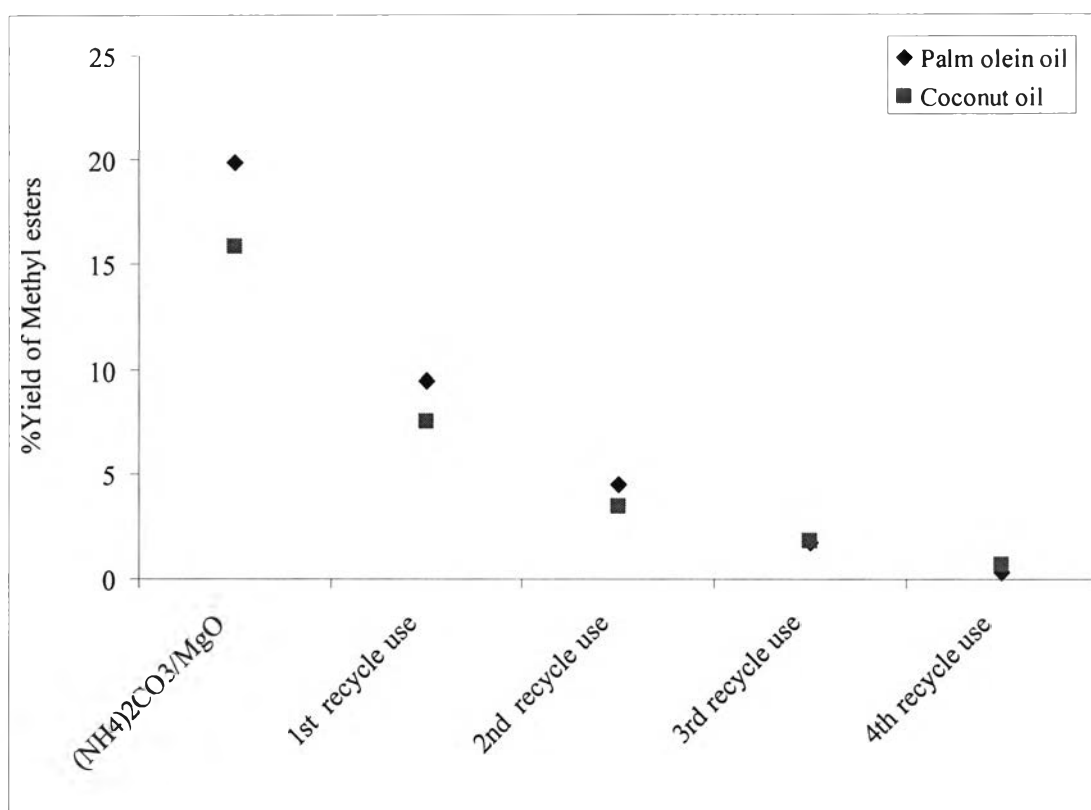
used for four times because alkali metal compounds are dissolvable in methanol which corroded the active site.



**Figure 4.13** Yield of methyl esters using 5 %wt of reused (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>/CaO, molar ratio of methanol to oil of 6:1, reaction temperature of 60°C, reaction time of 2 h and using THF as co-solvent.

Figure 4.13 shows effect of the activity of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>/CaO catalysts after repeatedly used on yield of methyl esters. The yield of methyl esters from palm olein oil decrease from 90% to 74% after used for one time and finally to 0.2% after used for the seven times. The yield of methyl esters from coconut oil decrease from 85% to 68% after used for one time and finally to 0.5% after used for the seven times. The activity of catalyst decrease which results from dissolve ammonium compound in the methanol because methanol removes the active sites of the catalyst. The analysis results are summarized in Tables D4 and D5 in Appendix D. Clairc et al. (2008) studied the reusability of

$\text{KNO}_3/\text{CaO}$  on biodiesel production. The experiment carried out with methanol to rapeseed oil ratio of 6:1, used 5% (w/w) catalyst to oil ratio for soybean oil, reaction temperature of  $60^\circ\text{C}$  and reaction time of 3 h. The results showed the comparing conversion after 1 cycle and 5 cycles of reaction for each of the active catalysts. In general, the conversions do not drop significantly after 5 cycles because active sites of  $\text{KNO}_3$  are dissolvable in methanol.



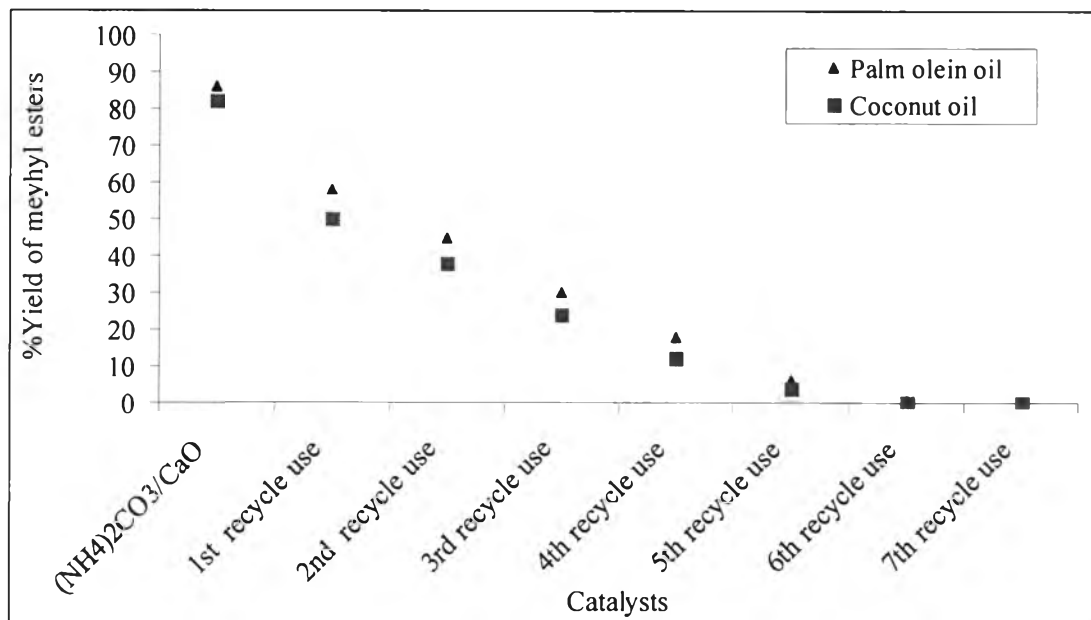
**Figure 4.14** Yield of methyl esters using 5 %wt of reused  $(\text{NH}_4)_2\text{CO}_3/\text{MgO}$ , molar ratio of methanol to oil of 6:1, reaction temperature of  $60^\circ\text{C}$ , reaction time of 2 h and using THF as co-solvent.

Figure 4.14 shows effect of the activity of  $(\text{NH}_4)_2\text{CO}_3/\text{MgO}$  catalysts after repeatedly used on yield of methyl esters. The yield of methyl esters from palm olein oil decrease from 20% to 9% after used for one time and finally to 0.3% after used for the four times. The yield of methyl esters from coconut oil decrease from 16% to 7% after used for one time and finally to 0.1% after used

for the four times. The analysis results were summarized in Tables D4 and D5 in Appendix D.

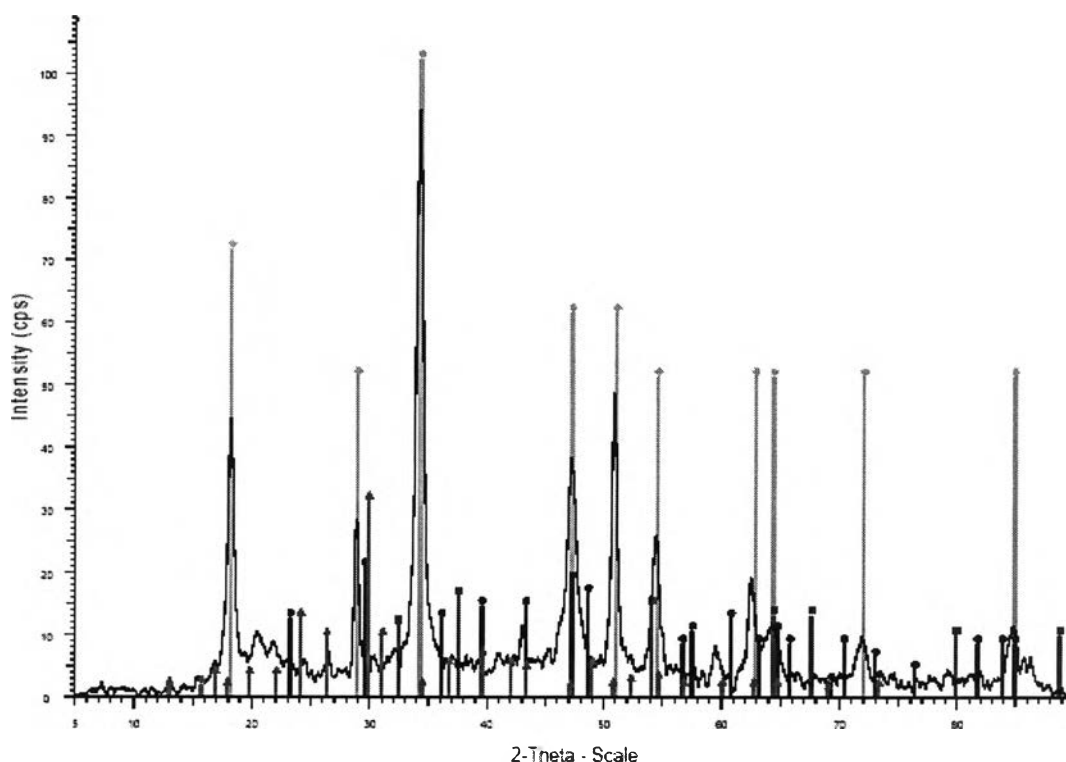
The results conclude that the 30% $(\text{NH}_4)_2\text{CO}_3/\text{CaO}$  catalysts are deactivated when used for seven cycles and  $(\text{NH}_4)_2\text{CO}_3/\text{MgO}$  catalysts are deactivated when used for four cycles because catalytic activity of catalyst decreased due to dissolved ammonium compound in methanol are corroded active site after wash deactivated catalyst with methanol.

This section investigated and compared activity of catalysts after repeatedly used. The reused catalysts were separated from product and will be used in the next experiment without washing catalyst with methanol. Study of deactivated catalysts were carried out with CaO modified with 30 %wt of  $(\text{NH}_4)_2\text{CO}_3$  as shown in Figure 4.15.

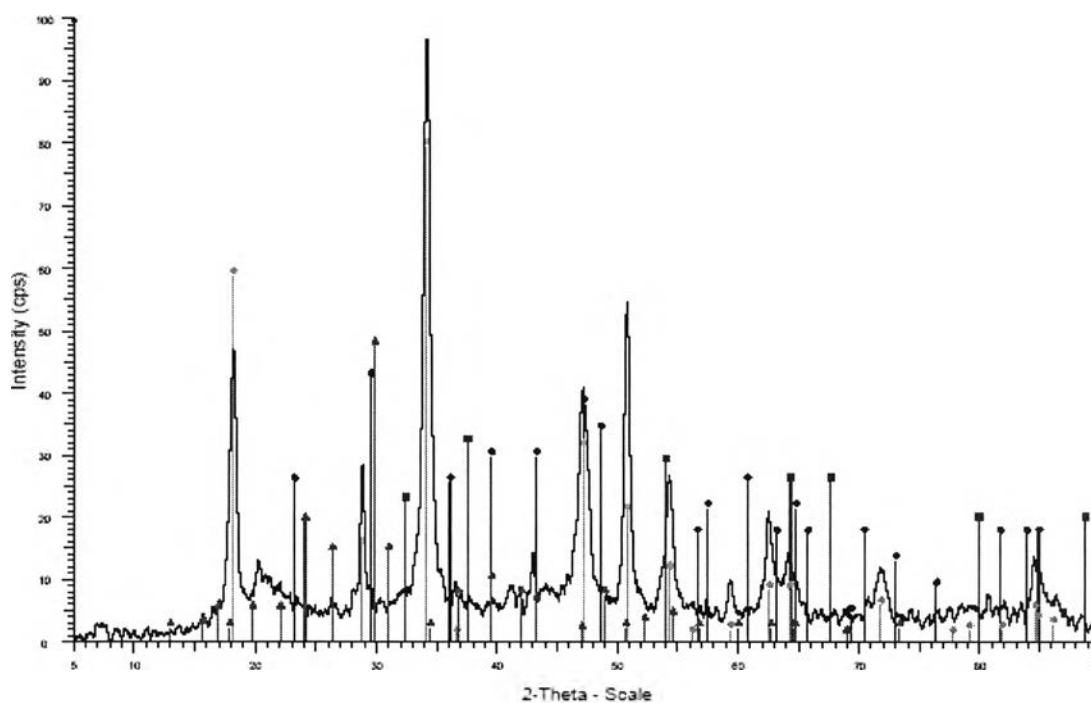


**Figure 4.15** Yield of methyl esters using 5 %wt of reused  $(\text{NH}_4)_2\text{CO}_3/\text{CaO}$  without washing with methanol, molar ratio of methanol to oil of 6:1, reaction temperature of  $60^\circ\text{C}$ , reaction time of 2 h and using THF as co-solvent.

Figure 4.15 shows effect of the activity of 30 %wt of  $(\text{NH}_4)_2\text{CO}_3/\text{CaO}$  catalysts after repeatedly used on yield of methyl esters, which obtained highest yield of methyl esters and rapidly decreased yield of methyl esters when used repeated catalyst in experiments. The yield of methyl esters from palm olein oil decrease from 86% to 58% after used for one time and finally to 0.1% after used for the seven times. The yield of methyl esters from coconut oil decrease from 82% to 50% after used for one time and finally to 0% after used for the seven times. The yield of methyl esters decrease because contaminating substance block the active site of catalysts which resulted to decrease yield of methyl esters. The analysis results are summarized in Table D6 in Appendix D.

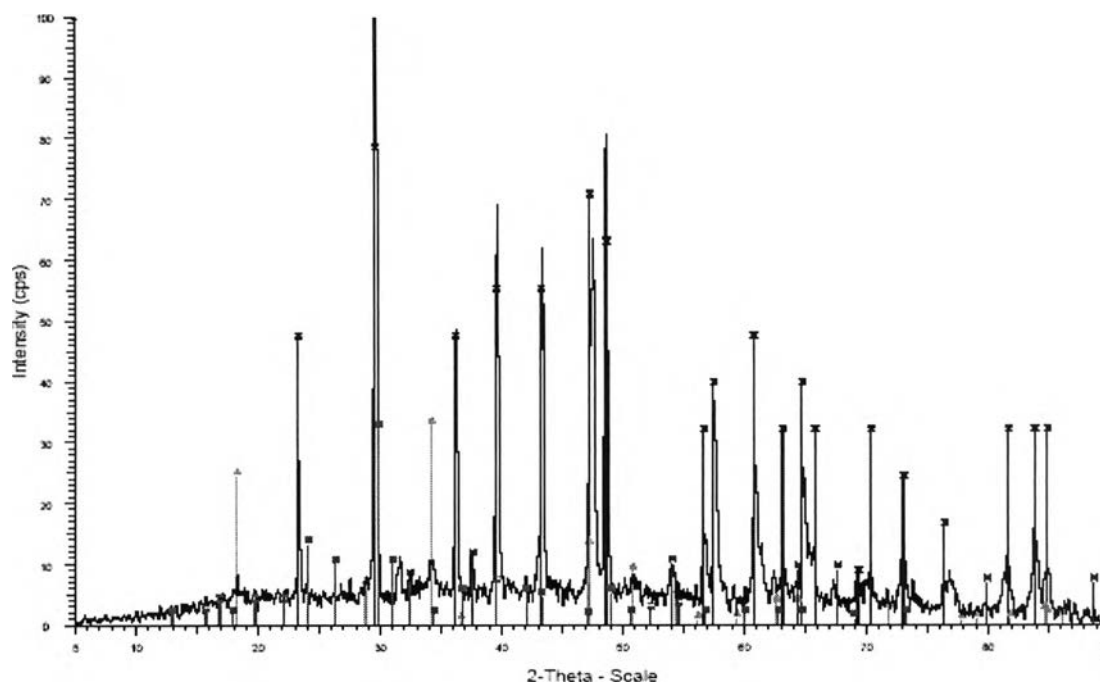


**Figure 4.16** XRD patterns of  $(\text{NH}_4)_2\text{CO}_3/\text{CaO}$  after used for one time of palm olein oil  $\blacklozenge$   $\text{Ca}(\text{OH})_2$   $\blacksquare$   $\text{CaO}$   $\bullet$   $\text{CaCO}_3/\text{CaO}\cdot\text{CO}_2$   $\blacktriangle$   $(\text{NH}_4)_2\text{CO}_3$

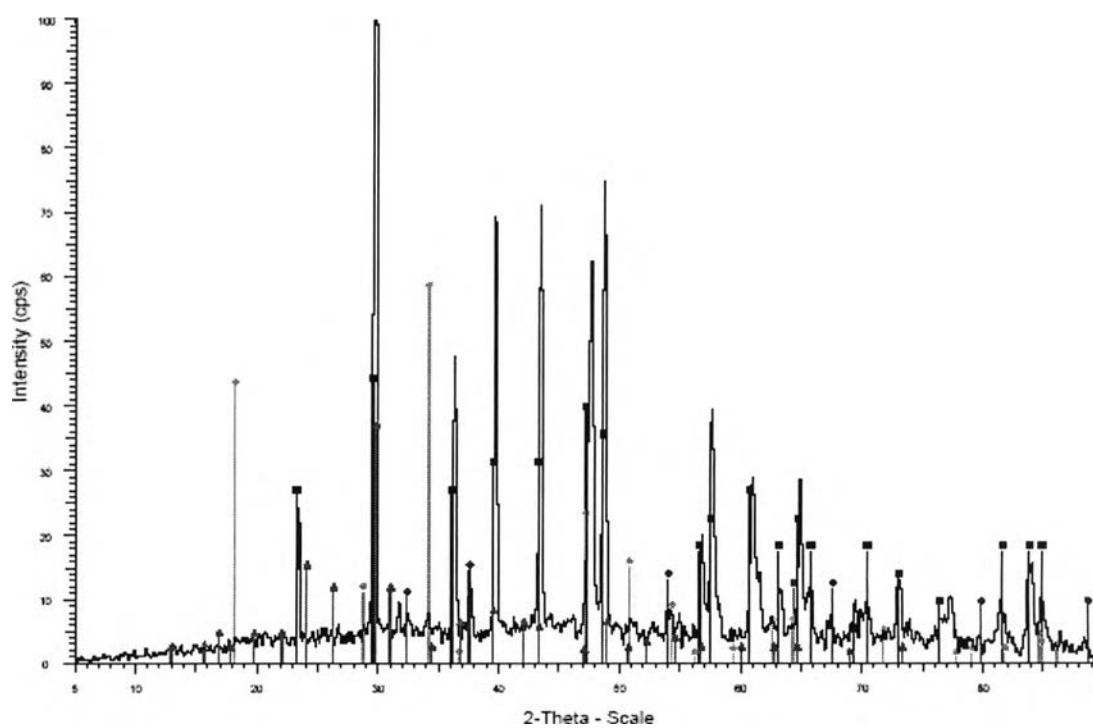


**Figure 4.17** XRD patterns of  $(\text{NH}_4)_2\text{CO}_3/\text{CaO}$  after used for one time of coconut oil  $\square$   $\text{Ca}(\text{OH})_2$   $\blacksquare$   $\text{CaO}$   $\bullet$   $\text{CaCO}_3/\text{CaO}\cdot\text{CO}_2$   $\triangle$   $(\text{NH}_4)_2\text{CO}_3$

Figures 4.16 and 4.17 show analyzed composition of  $(\text{NH}_4)_2\text{CO}_3/\text{CaO}$  catalyst with XRD analyzer after used for one time with palm olein oil and coconut oil in transesterification reaction at  $60^\circ\text{C}$  for 2 h. The results found that the presence of  $\text{Ca}(\text{OH})_2$  peaks on surface of catalyst. So  $\text{Ca}(\text{OH})_2$  formation obtained low amount of methyl esters and effected to rapidly deactivate catalysts.



**Figure 4.18** XRD patterns of  $(\text{NH}_4)_2\text{CO}_3/\text{CaO}$  after used for seven times of palm olein oil  $\diamond$   $\text{Ca}(\text{OH})_2$   $\blacksquare$   $\text{CaO}$   $\bullet$   $\text{CaCO}_3/\text{CaO}\cdot\text{CO}_2$   $\blacktriangle$   $(\text{NH}_4)_2\text{CO}_3$



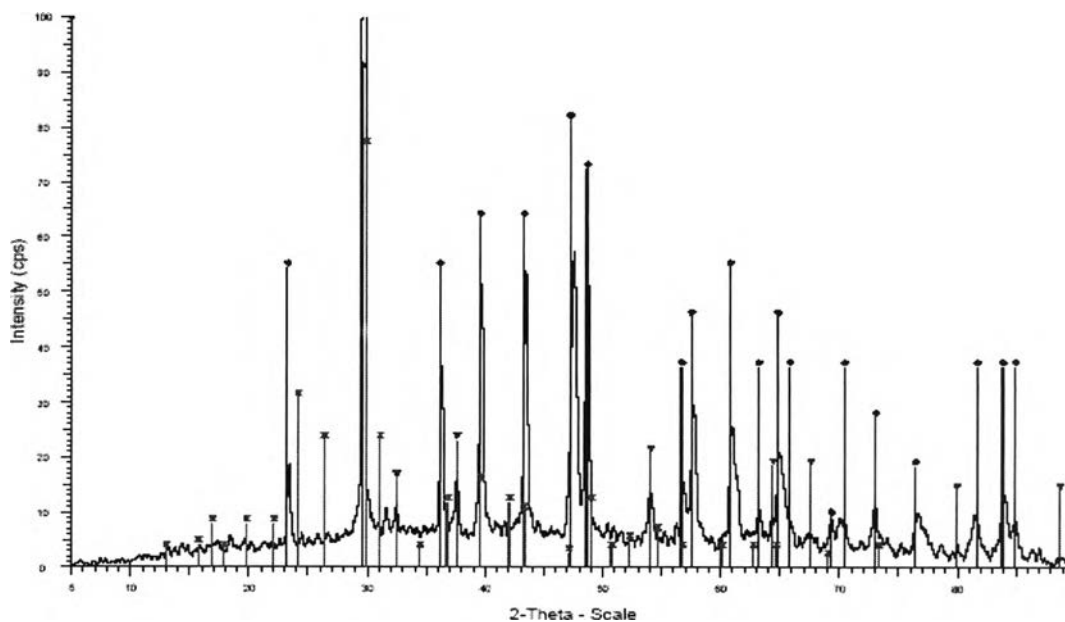
**Figure 4.19** XRD patterns of  $(\text{NH}_4)_2\text{CO}_3/\text{CaO}$  after used for seven times of coconut oil  $\diamond$   $\text{Ca}(\text{OH})_2$   $\blacksquare$   $\text{CaO}$   $\bullet$   $\text{CaCO}_3/\text{CaO}\cdot\text{CO}_2$   $\blacktriangle$   $(\text{NH}_4)_2\text{CO}_3$

Figures 4.18 and 4.19 show analyzed composition of  $(\text{NH}_4)_2\text{CO}_3/\text{CaO}$  catalyst with XRD analyzer after used for seven times with palm olein oil and coconut oil in transesterification reactions at  $60^\circ\text{C}$  for 2 h. The results found that the presence of  $\text{CaCO}_3/\text{CaO}\cdot\text{CO}_2$  peaks on surface of catalyst. So  $\text{CaCO}_3/\text{CaO}\cdot\text{CO}_2$  covered on surface of  $(\text{NH}_4)_2\text{CO}_3/\text{CaO}$  catalyst which effected to deactivate catalyst and obtained low amount of methyl esters.

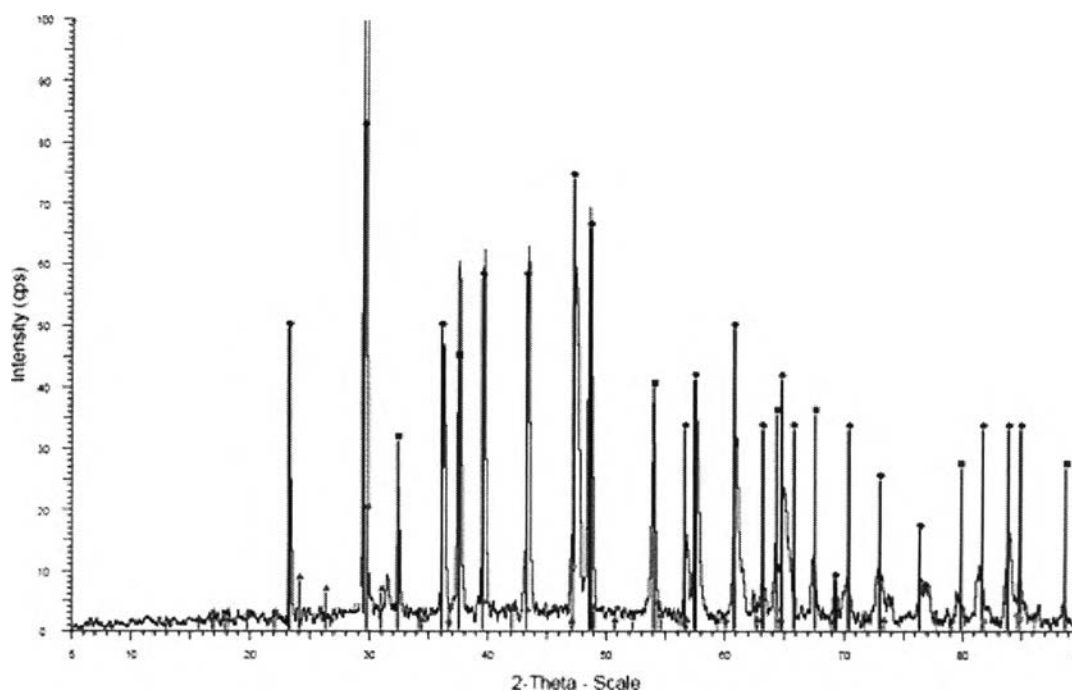
**Table 4.6** Comparing performance of used catalyst after used for seven times and calcined at  $600^\circ\text{C}$  for 3 h.

Catalysts	% Yield of methyl esters	
	Palm olein oil	Coconut oil
Fresh 30%wt $(\text{NH}_4)_2\text{CO}_3/\text{CaO}$	90	86
30%wt $(\text{NH}_4)_2\text{CO}_3/\text{CaO}$ after used for seven times	23	18

The results in Table 4.6 indicate that used 30 %wt of  $(\text{NH}_4)_2\text{CO}_3/\text{CaO}$  for seven times after that this catalyst is calcined at  $600^\circ\text{C}$  for 3 h. The results found that used catalyst for seven times obtained yield of methyl esters were 23% for palm olein oil and 18% for coconut oil. Furthermore, yield of methyl esters with reused catalyst obtained lower than fresh 30 %wt of  $(\text{NH}_4)_2\text{CO}_3/\text{CaO}$  catalyst because  $\text{Ca}(\text{OH})_2$  and  $\text{CaCO}_3/\text{CaO}\cdot\text{CO}_2$  covered surface of catalyst which effected to deactivate catalyst as shown in Figures 4.20 to 4.23. The analysis results were summarized in Table D6 in Appendix D.



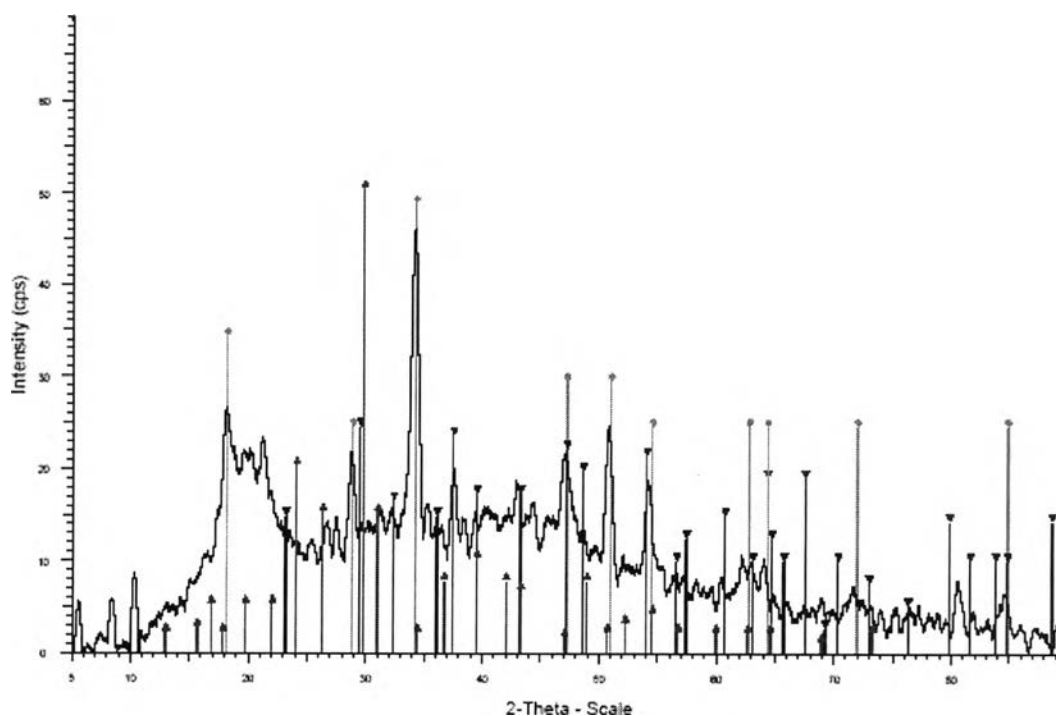
**Figure 4.20** XRD patterns of  $(\text{NH}_4)_2\text{CO}_3/\text{CaO}$  after used for seven times of palm olein oil and calcined  $600^\circ\text{C}$  for 3 h  $\diamond$   $\text{Ca}(\text{OH})_2$   $\blacksquare$   $\text{CaO}$   
 $\bullet$   $\text{CaCO}_3/\text{CaO}\cdot\text{CO}_2$   $\blacktriangle$   $(\text{NH}_4)_2\text{CO}_3$



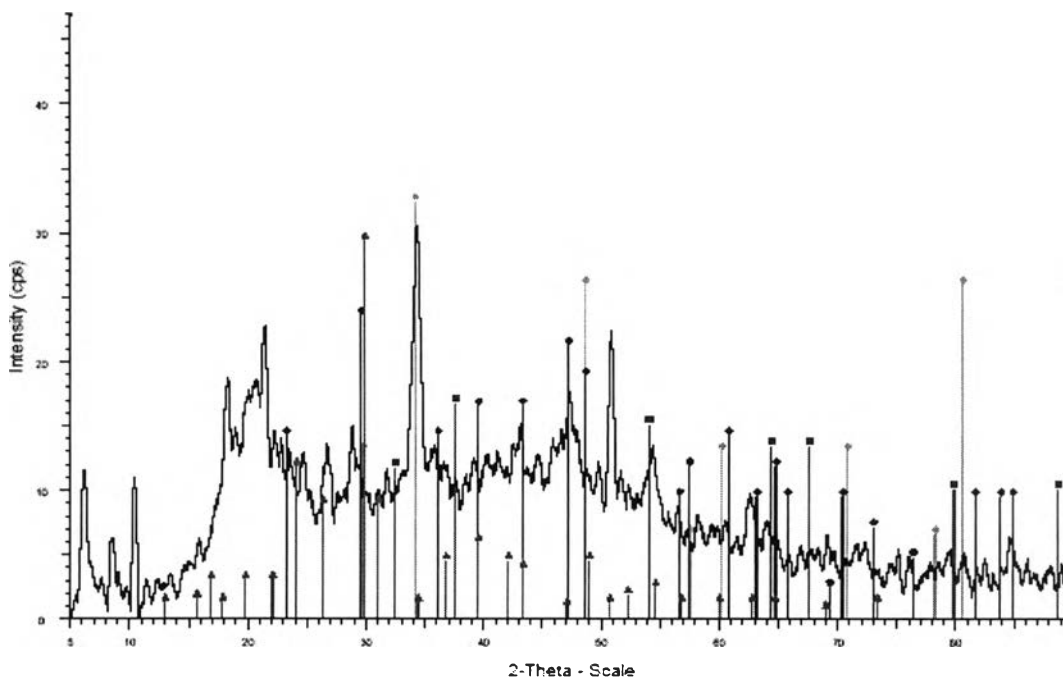
**Figure 4.21** XRD patterns of  $(\text{NH}_4)_2\text{CO}_3/\text{CaO}$  after used for seven times of coconut oil and calcined  $600^\circ\text{C}$  for 3 h  $\diamond$   $\text{Ca}(\text{OH})_2$   $\blacksquare$   $\text{CaO}$   
 $\bullet$   $\text{CaCO}_3/\text{CaO}\cdot\text{CO}_2$   $\blacktriangle$   $(\text{NH}_4)_2\text{CO}_3$



Figures 4.20 and 4.21 show analyzed composition of  $(\text{NH}_4)_2\text{CO}_3/\text{CaO}$  catalyst with XRD analyzer after used for seven times with palm olein oil and coconut oil in transesterification at  $60^\circ\text{C}$  for 2 h. The results found that  $\text{CaCO}_3/\text{CaO}\cdot\text{CO}_2$  and  $\text{CaO}$  covered on the surface of  $(\text{NH}_4)_2\text{CO}_3/\text{CaO}$  and  $\text{Ca}(\text{OH})_2$  was removed after the catalyst were calcined.



**Figure 4.22** XRD patterns of calcined  $(\text{NH}_4)_2\text{CO}_3/\text{CaO}$  after used for seven times of palm olein oil  $\blacklozenge$   $\text{Ca}(\text{OH})_2$   $\blacksquare$   $\text{CaO}$   $\bullet$   $\text{CaCO}_3/\text{CaO}\cdot\text{CO}_2$   $\blacktriangle$   $(\text{NH}_4)_2\text{CO}_3$



**Figure 4.23** XRD patterns of calcined  $(\text{NH}_4)_2\text{CO}_3/\text{CaO}$  after used for seven times of coconut oil  $\square$   $\text{Ca}(\text{OH})_2$   $\blacksquare$   $\text{CaO}$   $\bullet$   $\text{CaCO}_3/\text{CaO}\cdot\text{CO}_2$   $\blacktriangle$   $(\text{NH}_4)_2\text{CO}_3$

Figures 4.22 and 4.23 show XRD analysis result of used  $(\text{NH}_4)_2\text{CO}_3/\text{CaO}$  for seven times after that these catalysts were calcined at  $600^\circ\text{C}$  for 3 h and reacted with palm olein oil and coconut oil. The results found that used catalysts are deactivated because  $\text{Ca}(\text{OH})_2$  and  $\text{CaCO}_3/\text{CaO}\cdot\text{CO}_2$  cover surface of catalysts which effected to yield of methyl esters decrease.

The results conclude that the 30 %wt of  $(\text{NH}_4)_2\text{CO}_3/\text{CaO}$  catalysts are deactivated after used for seven times because catalytic activity of catalyst decreased due to dissolved ammonium compound in methanol which corroded active site after wash deactivated catalyst with methanol and after reaction the presence of  $\text{CaCO}_3/\text{CaO}\cdot\text{CO}_2$  and  $\text{Ca}(\text{OH})_2$  peaks on surface of catalyst. So  $\text{CaCO}_3/\text{CaO}\cdot\text{CO}_2$  and  $\text{Ca}(\text{OH})_2$  covered on surface of  $(\text{NH}_4)_2\text{CO}_3/\text{CaO}$  catalysts which effected to deactivate catalyst and obtain low amount of methyl esters.