

## CHAPTER IV

### RESULTS & DISCUSSION

#### 4.1 Physicochemical properties of catalysts

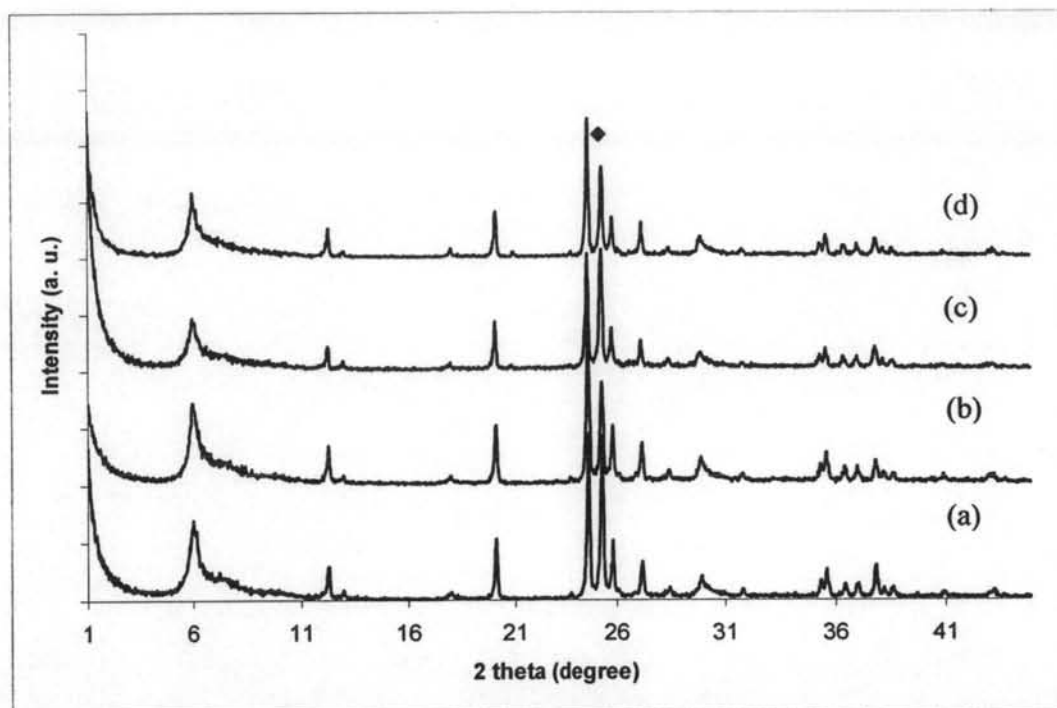
##### 4.1.1 Powder X-ray diffraction (XRD)

###### (a) ETS-10 catalyst

Figure 4.1 shows the XRD patterns of ETS-10 synthesized using colloidal silica or water glass solution as silica sources both as-synthesized and calcined samples, they proved to be mainly ETS-10 structure, together with co-crystallized anatase at 2-theta about 25.3. After calcination step, the ETS-10 phase still remained with slight increasing in intensity about 5%. In contrast, the intensity of anatase phase decreased about 28%. The main diffraction peaks exhibited at interplanar distances values ( $d$ ) of 0.361, 0.345 and 0.328 nm at 2-theta 24.7, 25.8 and 27.2, respectively. Moreover, the crystallinity of ETS-10 (CS) was higher than ETS-10 (WG) for about 25% regarding to the summation of peak area at 2-theta 24.65-27.5 as reported by Sivasanker, S. *et al.* [62].

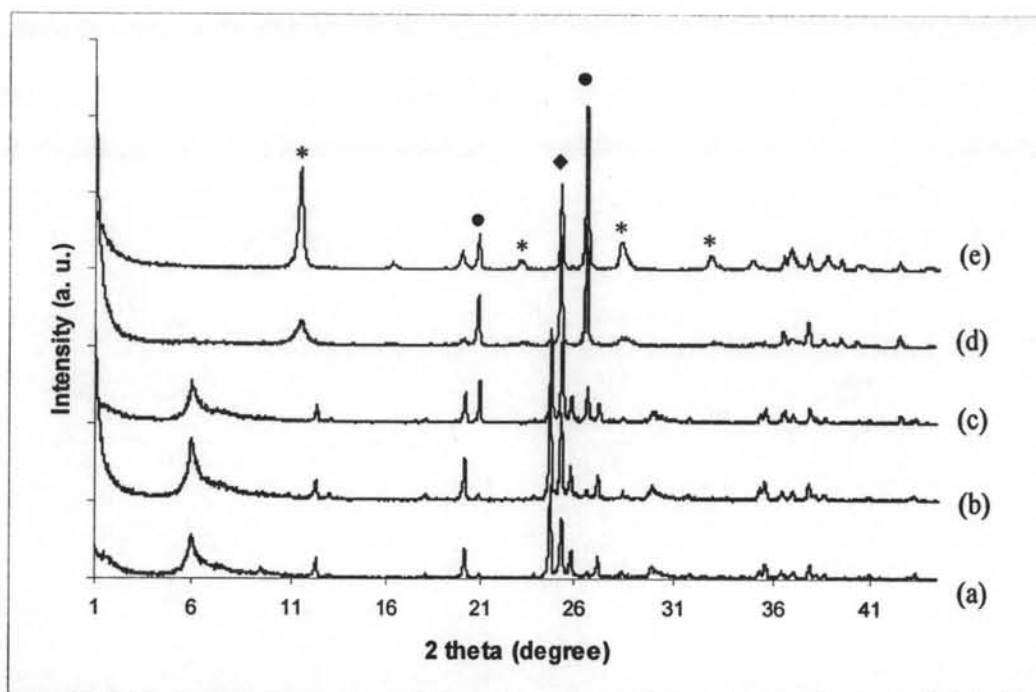
###### (b) Germanium substituted ETS-10

Germanium substituted ETS-10 or ETGeS-10 was also synthesized by direct method. A calculated amount of germanium oxide was added after TiO<sub>2</sub> dispersion in the prepared gel. The XRD patterns of ETGeS-10 at various mole ratios of Ge/Ti are shown in Figure 4.2.



**Figure 4.1** XRD patterns of as-synthesized ETS-10 (CS) (a), calcined ETS-10 (CS) (b), as-synthesized ETS-10 (WG) (c), and calcined ETS-10 (WG) (d). (◆ represents anatase phase).

It is obvious in Figure 4.2 that the structure of ETS-10 was affected by germanium loading. At a quite small loading of germanium for  $x$  equal to 0.15, there was no new phase detected but all peak intensities were enhanced. At higher germanium loadings where  $x$  equals to 0.5 up to 1.5, a peak was detected at  $2\theta$  of  $25^\circ$  and that was assigned to quartz. Upon increasing the germanium loading, the characteristic peaks of ETS-10 decrease in intensity along with the increase in peak intensities of quartz. When  $x$  equals to 1.0, the characteristic peaks of ETS-10 structure disappear completely. A set of new peaks at  $2\theta$  near  $11^\circ$ ,  $23^\circ$ ,  $29^\circ$ , and  $33^\circ$ , may include in partial of the intense peak at  $2\theta$   $26.7^\circ$ , were the most pronounced in intensity when  $x$  equals to 1.5. Those peaks belong to an unidentified crystalline material. Other two small peaks at  $2\theta$  of  $20^\circ$  and  $21^\circ$  were unidentified either.



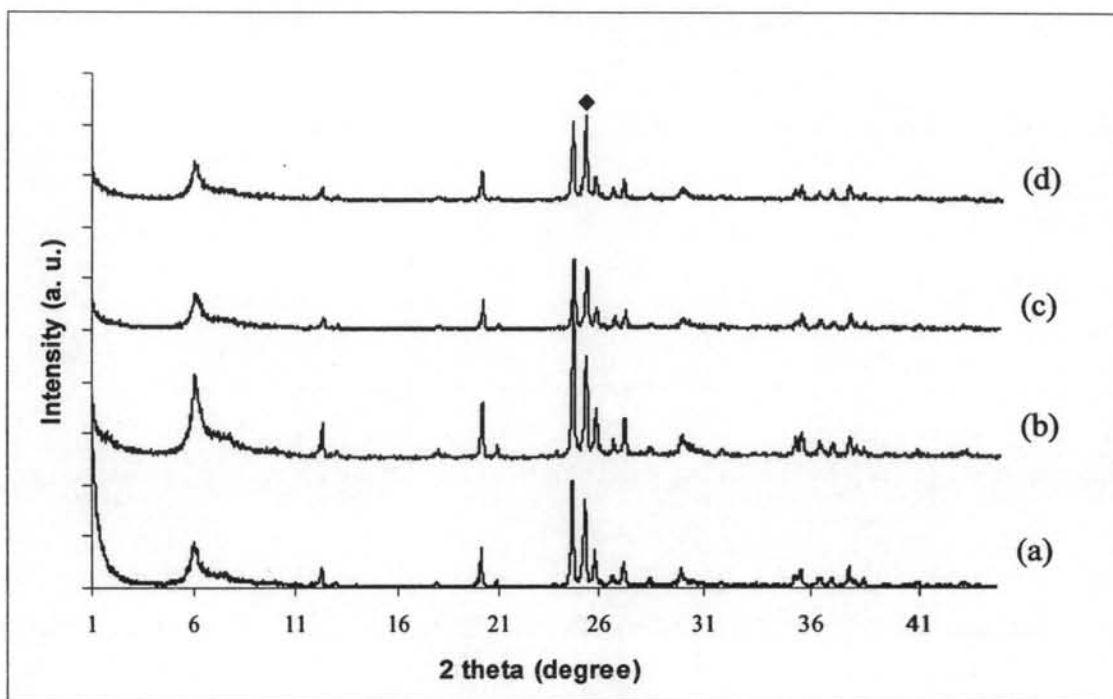
**Figure 4.2** XRD patterns of calcined ETS-10 (CS) (a),  $ET(Ge)_xS-10$ , where  $x$  is 0.15 (b), 0.5 (c), 1.0 (d), and 1.5 (e). (• represents quartz impurity phase and ◆ represents anatase phase and \* for unidentified crystalline phases).

### (c) Na-loaded ETS-10

After the synthesis, basic strength of catalyst was modified by two methods. The first one was ion-exchange with sodium ions to prepare sodium-exchanged ETS-10 (NaETS-10) catalyst and the second one was incipient-wetness impregnation with sodium precursors, sodium acetate or sodium hydroxide to produce sodium-impregnated ETS-10 denoted as NaOAc/ETS-10 and NaOH/ETS-10, respectively.

XRD patterns of various Na-loaded ETS-10 catalysts are shown in Figure 4.3. All of modified materials also maintain characteristic peaks of the ETS-10 structure with lower crystallinity. Compared to the original ETS-10 (a), the diffraction peaks of the NaETS-10 sample, prepared by sodium ion-exchange method, slightly increases in intensity, *i.e.* about 24%. The modification of ETS-10 with sodium acetate and sodium hydroxide followed by calcination caused the changes in XRD peak intensities. The XRD peak intensities of NaOAc/ETS-10 and NaOH/ETS-10

decrease about 30% because of the interaction of alkali metal species with ETS-10. No new crystalline phase was detected. The sample prepared by ion-exchange method presents the highest crystallinity compared with other samples.



**Figure 4.3** XRD patterns of calcined ETS-10 (CS) (a), NaETS-10 (b), NaOAc/ETS-10 (c), and NaOH/ETS-10 (d). (◆ represents for anatase).

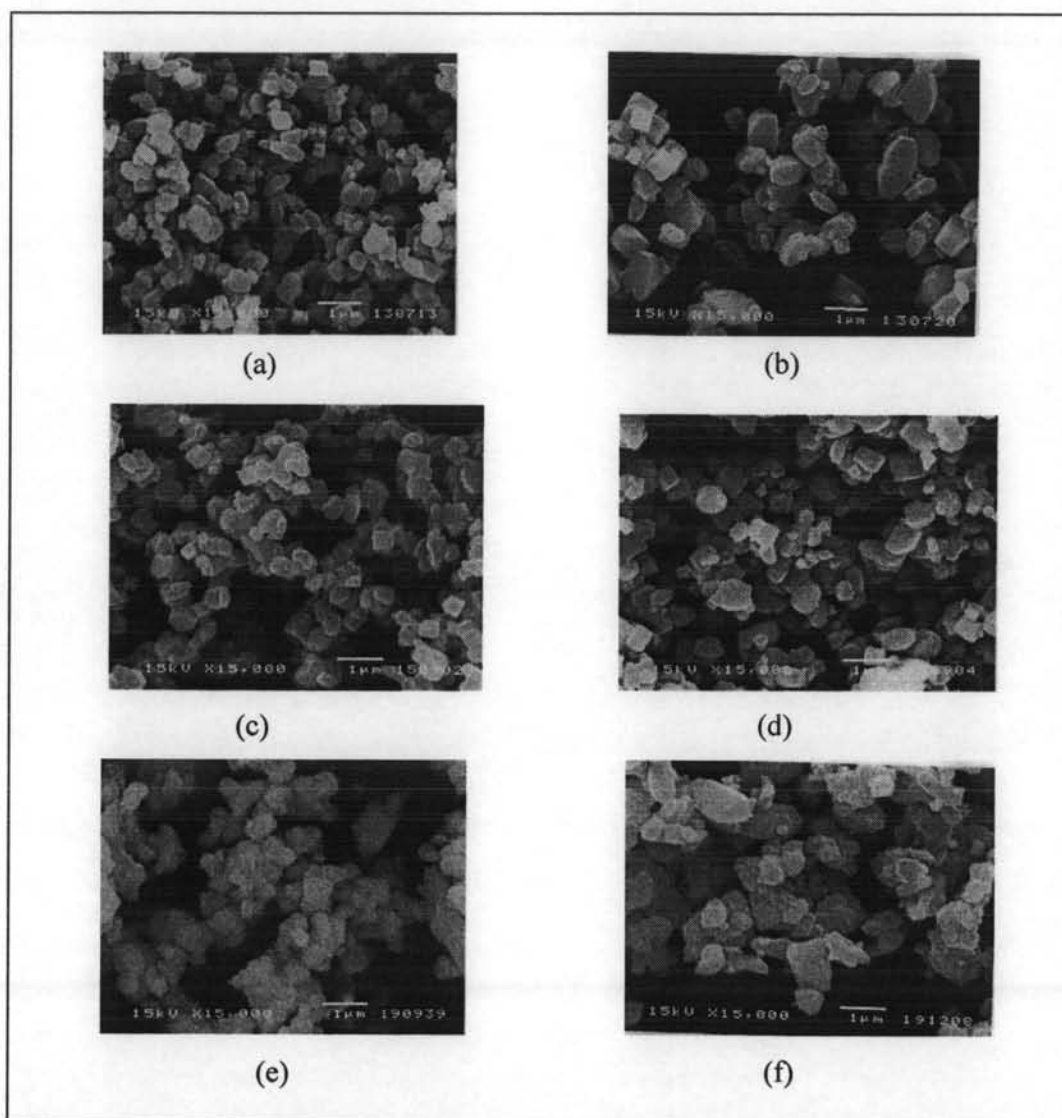
#### 4.1.2 Scanning electron microscopy (SEM)

##### (a) ETS-10 and ETGeS-10 catalyst

SEM images of calcined ETS-10 (CS), ETS-10 (WG), and  $\text{ET}(\text{Ge})_x\text{S-10}$  where  $x$  is 0.15-1.5 are shown in Figure 4.4. It indicates that both ETS-10 (CS) and ETS-10 (WG) have the morphology as quasi-cubic shape and the particles tend to agglomerate toward the elongated crystal assembly. The particle size of ETS-10 synthesized from colloidal silica was in the range of 300-500 nm whereas, ETS-10 synthesized from water glass solution has larger particle sizes, *i.e.* about 500-700 nm in size.

The particle morphology of  $\text{ET}(\text{Ge})_x\text{S-10}$  ( $x = 0.15$  and  $0.5$ ) is similar to that of ETS-10 (CS) and ETS-10 (WG) and their particle sizes are about 300-500 nm, which are the same as those of ETS-10 (CS). When  $x$  equals 1.0 or 1.5, SEM images show some chunk particles other than cubic like ETS-10 particles due to

significant amount of those impurities including quartz and anatase that was confirmed by their XRD patterns.

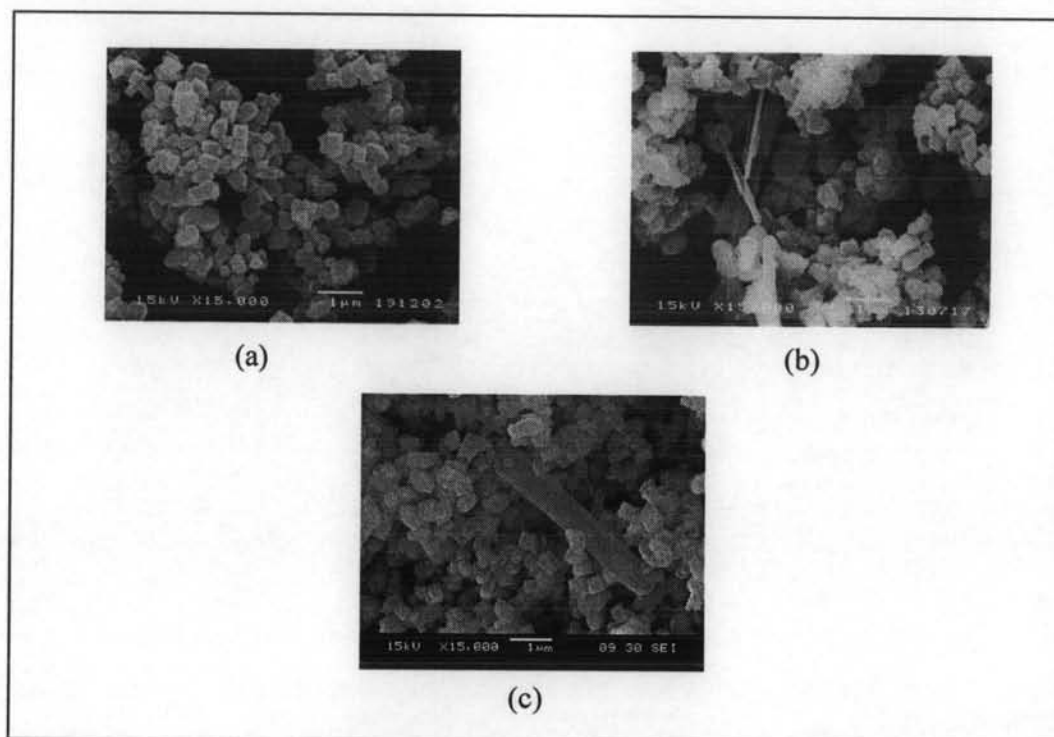


**Figure 4.4** SEM images of calcined ETS-10 (CS) (a), ETS-10 (WG) (b),  $ET(Ge)_xS-10$  where  $x$  is 0.15 (c), 0.5 (d), 1.0 (e), and 1.5 (f).

#### (b) Na-loaded ETS-10

SEM images of calcined NaETS-10, NaOAc/ETS-10, and NaOH/ETS-10 are shown in Figure 4.5. The same morphology and particle size as parent ETS-10 were obtained for calcined NaETS-10. In addition, it was clear that no other phase occurred after exchange ETS-10 with sodium ions. In the cases of sodium impregnated ETS-10 (NaOAc/ETS-10 and NaOH/ETS-10), no important difference

was observed between the parent ETS-10 and Na-impregnated samples, except for the presence of rectangular shape of sodium species indicating not highly dispersed sodium precursors.



**Figure 4.5** SEM images of calcined NaETS-10 (a), NaOAc/ETS-10 (b), and NaOH/ETS-10 (c).

#### 4.1.3 Sorption properties

ETS-10 and metal doped samples exhibit a  $N_2$  adsorption isotherm of type I, characteristic of micropores as shown in Figure A-1 (appendices). Some physical properties derived from the adsorption isotherms of ETS-10, ETGeS-10 and Na-loaded ETS-10 catalysts are compiled in Table 4.1. BET specific surface areas of ETS-10 prepared from colloidal silica is higher than that from water glass solution and similar trend for their external surface areas. Both of them have the same micropore volume of  $0.13 \text{ cm}^3/\text{g}$  and the same average pore diameter of 0.6 nm. Germanium substituted ETS-10 or ETGeS-10 samples exhibit lower BET specific surface area compared with ETS-10 without germanium. The higher loading of germanium, the lower the BET specific surface area is. However, the samples with low loadings of germanium,  $x$  is 0.15-0.5, maintain BET specific surface area values

in the range of typical porous materials. The decrease in BET specific surface area was drastic for the samples with higher germanium loading indicating the collapse of porous structure of ETS-10 that is in agreement with their XRD results. All samples exhibit quite low external surface area as a usual behavior of microporous zeolites. Germanium loading even results in no change of the external surface area except the high loading with  $x$  equal to 1.5. The slight decrease in pore volume of ETGeS-10 catalyst was also observed, it was in the same trend as the surface area.

NaETS-10, NaOAc/ETS-10 and NaOH/ETS-10 also exhibit the type I adsorption isotherm as the parent sample. The BET specific surface area significantly decreases about 40% and 37% after Na-exchanged and Na-impregnation followed by calcination, respectively. The decrease of surface area results from the agglomeration of sodium oxide as reported by Ziolek, M. *et al.* [62] and confirmed by SEM. Moreover, the pore volume of Na-loaded slightly decreases. It may be concerned with the sodium species transfer into pore structure. The adsorption properties are affected in the same extent by types of sodium precursors and method of loading.

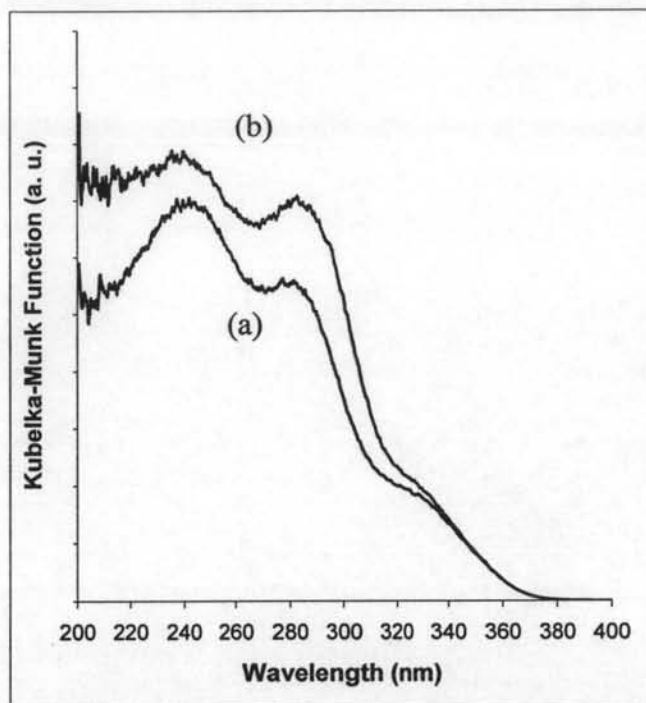
**Table 4.1** Some physical properties of ETS-10, ETGeS-10 and Na-loaded ETS-10 catalysts

Sample	BET specific surface area, $a_s$ (m <sup>2</sup> /g)	External surface area, $a_{ext}$ (m <sup>2</sup> /g)	Micropore volume, $v_p$ (cm <sup>3</sup> /g)	Average pore diameter, $d_p$ (nm)
ETS-10 (CS)	398	10	0.13	0.60
ETS-10 (WG)	312	7	0.13	0.60
ET(Ge) <sub>x</sub> S-10				
x = 0.15	291	10	0.12	0.60
x = 0.5	244	10	0.10	0.60
x = 1.0	25.8	8	0	0.60
x = 1.5	2	0.5	0	0.90
NaETS-10	239	5	0.10	0.60
NaOAc/ETS-10	255	5	0.11	0.60
NaOH/ETS-10	249	6	0.11	0.60

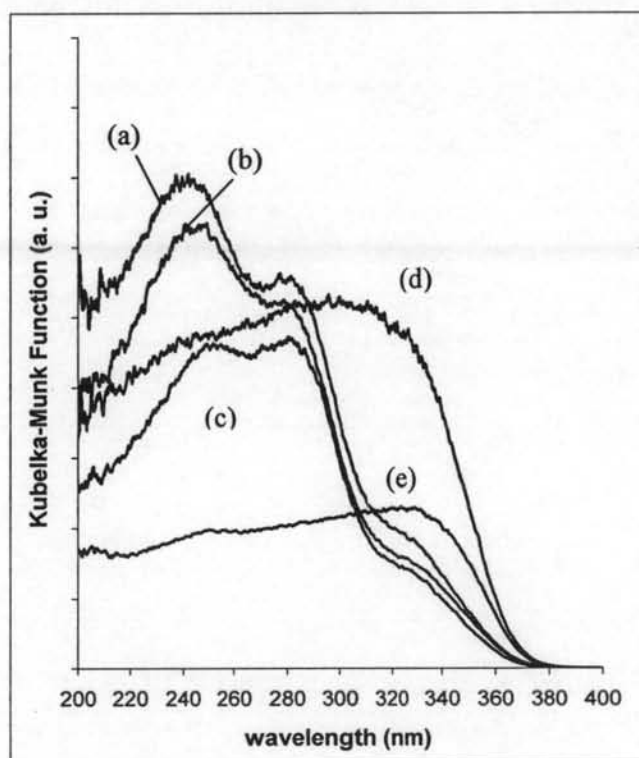
#### 4.1.4 Diffuse-reflectance-ultraviolet spectroscopy (DR-UV)

Form of titanium in ETS-10 can be divided into three types. The first one is pentahedral form ( $O=TiO_4^{-4}$ ) at extra-framework position. The second is octahedral form ( $TiO_6^{-8}$ ) and the last one is anatase ( $TiO_2$ ). The absorption spectra of normal and modified ETS-10 samples are shown in Figures 4.6-4.8. In Figure 4.6, three UV absorption bands at 240, 280 and 330 nm attributed to the O2p to Ti3d charge transfer (CTT) were observed. The bands at 240 and 280 were assigned to the charge transfer from Si,Ti-linking and Ti,Ti-linking oxygen to Ti, respectively, according to Tasumi, T. *et al.* [16]. The band at 215 nm typically assigned to framework was not observed. This is the difference from other zeolite-structure titanosilicates like TS-1, which usually exhibits the band at 215 nm. The band at 330 nm is assigned to anatase and it was confirmed by XRD diffraction peak at 2-theta about 25.3.

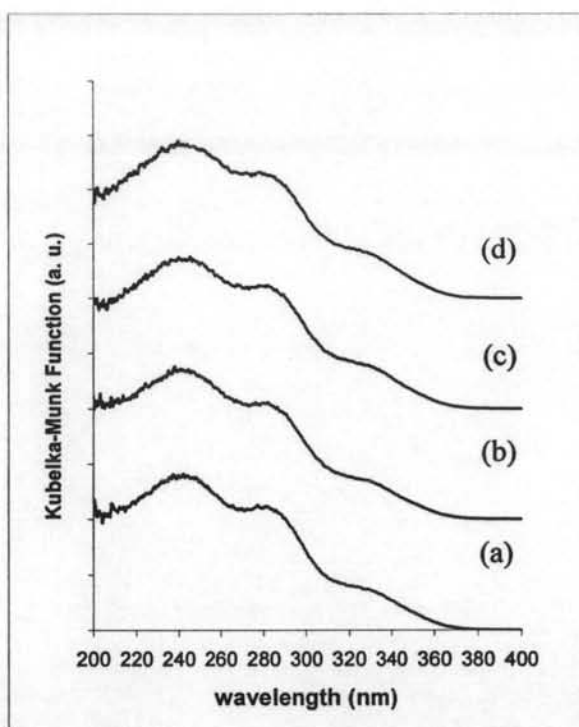




**Figure 4.6** DR-UV spectra of calcined ETS-10 (CS) (a), and ETS-10 (WG) (b).



**Figure 4.7** DR-UV spectra of calcined ETS-10 (CS) (a), ET(Ge)<sub>x</sub>S-10, where x is 0.15 (b), 0.5 (c), 1.0 (d), and 1.5 (e).



**Figure 4.8** DR-UV spectra of calcined ETS-10 (CS) (a), NaETS-10 (b), NaOAc/ETS-10 (c), and NaOH/ETS-10 (d).

ET(Ge)<sub>x</sub>S-10 samples ( $x = 0.15$  and  $0.5$ ) still display three absorption bands like normal ETS-10 without germanium, whereas the spectra of ET(Ge)<sub>x</sub>S-10 ( $x = 1$  and  $1.5$ ) show only a convoluted broad band with a maximum at 330 nm. It indicates the significant amount of anatase in the high germanium loaded samples.

From DR-UV spectra in Figure 4.8, it is obvious that Na-modified catalysts both from ion-exchange (b) and from impregnation methods (c and d) show three absorption bands located in the same wavelength range and with the comparable intensity. This result indicates that sodium species do not have any effect on the titanium species either in quantity or in their environment.

#### 4.1.5 Scanning electron microscopy-energy dispersive X-ray

SEM-EDX was used in the measurement of germanium amount in germanium substituted ETS-10 catalysts compared to the amount in gel and the results are shown in Table 4.2. The germanium contents in ET(Ge)<sub>x</sub>S-10 ( $x = 0.15$  and

0.5) products are higher than in starting gel. The higher loading in gel, the higher content was incorporated in catalyst.

**Table 4.2** Germanium contents in ETGeS-10 catalysts

Sample	Germanium content (wt%)	
	in gel	in product
<b>ET(Ge)<sub>x</sub>S-10</b>		
x = 0.15	0.57	0.60
x = 0.5	1.88	2.15
x = 1.0	3.60	9.30
x = 1.5	5.27	14.20

#### 4.1.6 Elemental ratios in ETS-10 and modified catalysts

The titanium contents in ETS-10 and modified catalysts were determined by ICP-AES, whereas amounts of sodium and potassium were obtained by AAS. The analysis data are compiled in Table 4.3. ETS-10 prepared from colloidal silica has slightly lower Si/Ti and significantly lower Na/Ti mole ratios than in ETS-10 prepared from water glass but they have the same K/Ti mole ratio. The silica source plays an effect mostly on Na/Ti mole ratio in those catalysts.

**Table 4.3** Elemental analysis of ETS-10, ETGeS-10 and Na-loaded ETS-10

Sample	Si/Ti <sup>a</sup>	Na <sup>b</sup> /Ti	K <sup>b</sup> /Ti
ETS-10 (CS)	3.51	0.51	0.19
ETS-10 (WG)	4.09	0.66	0.19
ET(Ge) <sub>x</sub> S-10			
x= 0.15	3.40	0.58	0.19
x= 0.5	3.71	0.41	0.26
x= 1.0	3.30	0.24	0.23
x= 1.5	3.18	0.29	0.26
NaETS-10	3.63	0.60	0.14
NaOAc/ETS-10	3.24	0.52	0.21
NaOH/ETS-10	3.45	0.58	0.22

<sup>a</sup> from ICP-AES analysis<sup>b</sup> from AAS analysis

The Si/Ti mole ratios in all ET(Ge)<sub>x</sub>S-10 samples are nearly the same as in ETS-10 sample. The Na/Ti mole ratio in ET(Ge)<sub>x</sub>S-10 (x = 0.15) is higher than other ET(Ge)<sub>x</sub>S-10 samples which have not different Na/Ti mole ratios. The values of Na/Ti ratio in ET(Ge)<sub>x</sub>S-10 (x = 0.15) is higher than in the analogous ETS-10 (CS) sample. With increasing the germanium loading in the synthesis course results in lower Na/Ti ratios in ET(Ge)<sub>x</sub>S-10 when x is in the range of 0.5-1.5. As previously described, germanium caused the structure collapsed, results in less amount of negatively charged octahedral titanium species and more neutrally charged anatase. Thus less uptake of Na in the structure is account for the decrease in Na/Ti ratio compared to ETS-10 without germanium. The values of K/Ti ratios were found at a trace amount about 0.1-0.3 in all samples with the deviation of ±0.04. The difference is hardly evaluated due to too low values.

NaETS-10 contains more Na/Ti mole ratio than the mother ETS-10 (CS) while NaOAc/ETS-10 and NaOH/ETS-10 contain the similar amount to the unmodified ETS-10. The modifying method by ion exchange can provide by considerably larger sodium uptake than the wetness impregnation because an amount of 15 mmol/g catalyst of Na precursor was used for ion exchange while 0.5 mmol/g catalyst was used for wetness impregnation. The latter case is quite small and accounted for no change of Na/Ti ratio compared to the sodium-unloaded ETS-10.

## **4.2 Catalytic activity of ETS-10 in transesterification reaction**

### **4.2.1 Effect of silica sources**

The catalytic activities of ETS-10 catalysts prepared from different silica sources methods in transesterification reaction of palm oil are shown in Table 4.4. MO, MP, ML and MS are abbreviations of methyl oleate, methyl palmitate, methyl linoleate, and methyl stearate. Comparing to the blank test, both ETS-10 samples are slightly active for transesterification of palm oil to yield methyl ester. ETS-10 (CS) provides 3.0% higher total methyl ester yield than ETS-10 (WG), and 4.5% higher total methyl ester yield than the blank test. This is due to smaller particle size of ETS-10 (CS) catalyst, resulting in higher specific surface area than ETS-10 (WG). The ester distribution in all cases are in the order of methyl oleate  $\approx$  methyl palmitate  $\gg$  methyl linoleate  $>$  methyl stearate following the amount of corresponding fatty acid composition in the starting palm oil. In all cases only trace amounts of glycerol of less than 0.01 wt% were remained. Comparing with the previous study [28], the ETS-10 was chosen to catalyze the soybean oil transesterification. The reaction was performed in seal tube reactor at various temperatures. The results showed oil conversion to methyl esters in range of 95-84% were achieved over ETS-10, KETS-10 and CsETS-10 catalysts.

**Table 4.4** The catalytic activities of ETS-10 catalysts prepared from different silica sources methods in transesterification reaction of palm oil

Catalyst	Methyl ester yield (wt%)				Total yield (wt%)	MO:MP:ML:MS wt ratio
	MO	MP	ML	MS		
None	1.32	1.26	0.39	0.10	3.01	13:13:4:1
ETS-10 (CS)	3.50	3.12	0.61	0.30	7.53	11:10:2:1
ETS-10 (WG)	2.03	1.85	0.43	0.22	4.53	9:9:2:1

Reaction condition: 10 wt% catalyst, MeOH to oil mole ratio of 9:1 at 120°C, and for 24 h

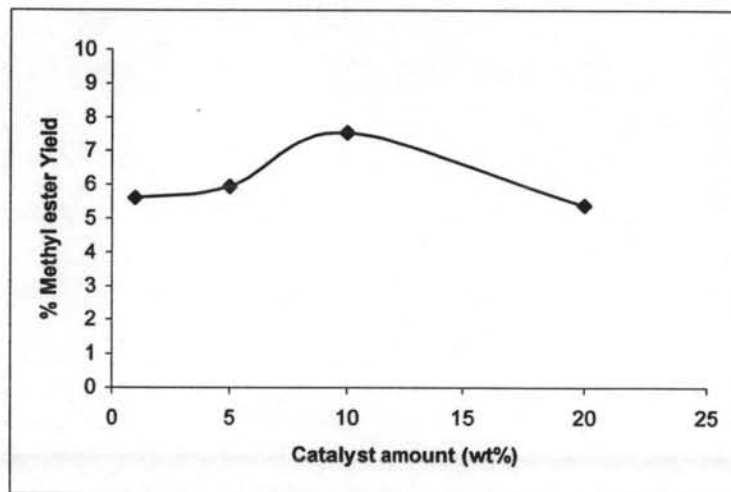
#### 4.2.2 Effect of catalyst amount

Amounts of 1, 5, 10 and 20 wt% of catalysts to reactant mixture were varied to find out the most appropriate one and the catalytic activities of ETS-10 (CS) at various catalyst amounts in the transesterification of palm oil are shown in Table 4.5. The corresponding plot of methyl ester yield versus catalyst amount is shown in Figure 4.11. The catalyst amounts of 1 and 5 wt% provide almost the same methyl ester yield. The increased yield was obtained by increasing the catalysts amount from 5 to 10 wt% the lowered yield was surprisingly obtained when the catalyst amount was increased to 20 wt%. The reason may be that the products can be adsorbed on the overloaded catalyst. In all cases, the ester distribution is the same and in the order of methyl oleate  $\approx$  methyl palmitate  $\gg$  methyl linoleate  $>$  methyl stearate. There is no doubt about the analysis technique due to the internal standard, eicosane, was used in the correction of the injection volume of GC samples.

**Table 4.5** The catalytic activities of ETS-10 (CS) at various catalyst amounts in the transesterification of palm oil

Catalyst amount (wt%)	Methyl ester yield (wt%)				Total yield (wt%)	MO:MP:ML:MS wt ratio
	MO	MP	ML	MS		
1	2.56	2.31	0.49	0.25	5.60	10:9:2:1
5	2.73	2.44	0.53	0.25	5.95	10::9:2:1
10	3.50	3.12	0.61	0.30	7.53	11:10:2:1
20	2.36	2.34	0.46	0.22	5.38	10:10:2:1

Reaction condition: MeOH to oil mole ratio of 9:1 at 120°C, and for 24 h



**Figure 4.9** The plot of methyl ester yield versus catalyst amount of ETS-10 (CS).

#### 4.2.3 Effect of methanol to oil mole ratio

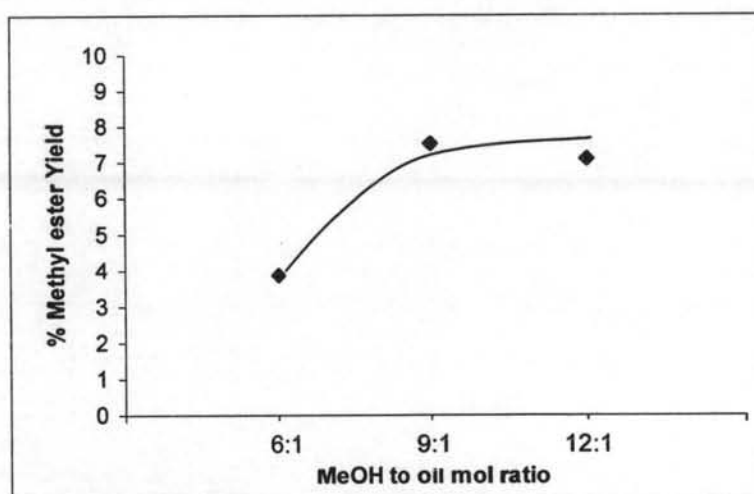
The stoichiometric molar ratio requires three moles of alcohol and one mol of triglyceride to produce three moles of ester and one mol of glycerol, but in practice the excess amount of alcohol in transesterification of vegetable oils is needed in order to drive the reaction towards completion and produce more methyl esters as products. The catalytic activities of ETS-10 (CS) in the transesterification of palm oil at various ratios of methanol to oil are shown in Table 4.6 and the corresponding plot of methyl ester yield versus ratios of methanol to oil is shown in Figure 4.10. The various ratios methanol to oil were used at 6:1, 9:1 and 12:1. By increasing the methanol to oil mol ratio from 6:1 to 9:1, the methyl ester yield considerably

increased from almost 4 to about 7 wt%. From the data in Table 4.6 the methanol to oil ratio of 9:1 is the most appropriate one to give the highest yield of methyl ester. There is no significant difference between the ratios of 9:1 and 12:1. The product distribution is still in the order of methyl oleate  $\approx$  methyl palmitate  $\gg$  methyl linoleate  $>$  methyl stearate.

**Table 4.6** The catalytic activity of ETS-10 (CS) in the transesterification of palm oil at various ratios of methanol to oil

MeOH to Oil mole ratio	Methyl ester yield (wt%)				Total yield (wt%)	MO:MP:ML:MS wt ratio
	MO	MP	ML	MS		
6:1	1.67	1.66	0.33	0.20	3.86	10:10:2:1
9:1	3.50	3.12	0.61	0.30	7.53	11:10:2:1
12:1	3.08	3.03	0.67	0.31	7.09	9:9:2:1

Reaction condition: 10 wt% catalyst, at 120°C, and for 24 h



**Figure 4.10** The plot of methyl ester yield over ETS-10 (CS) versus mole ratios of methanol to oil.

#### 4.2.4 Effect of reaction time

The dependence of methyl esters yield on reaction time was also investigated. The catalytic activities of ETS-10 (CS) in the transesterification of palm oil at different reaction time are shown in Table 4.7. The reaction time was varied in

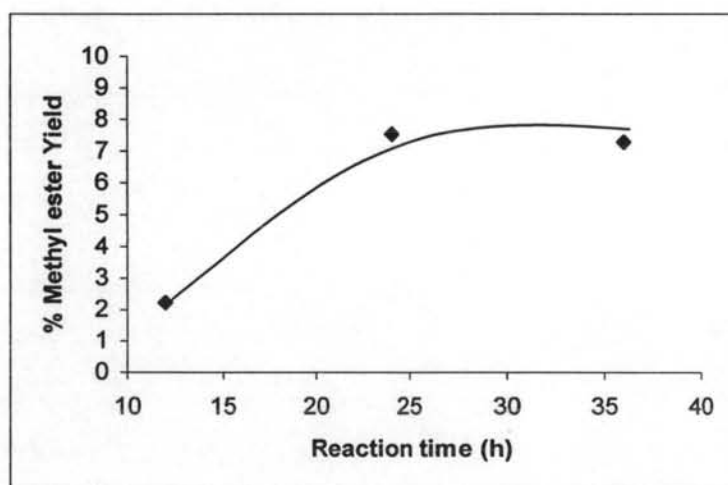


the range of 12-36 h. It is obvious that the reaction time of 12 h is not enough for the completion of the transesterification of palm oil at 120 °C. The reaction time of 24 h makes the yield of methyl ester reach the highest value about 7 wt% with the highest selectivities to methyl oleate and methyl palmitate. Extension of reaction time over 24 h does not make the increase in the ester yield. It indicates that the reaction is complete within 24 h. Considering the ester distribution, it is a drastic difference for the reaction time of 12 h and others. The reaction time of only 12 h is not enough for some triglycerides causing lower yield of corresponding methyl esters. Only trace amounts of glycerol of less than 0.01 wt% were remained.

**Table 4.7** The catalytic activities of ETS-10 (CS) in the transesterification of palm oil for different reaction time

Reaction time (h)	Methyl ester yield (wt%)				Total yield (wt%)	MO:MP:ML:MS wt ratio
	MO	MP	ML	MS		
12	0.83	0.81	0.39	0.18	2.21	4:4:2:1
24	3.50	3.12	0.61	0.30	7.53	11:10:2:1
36	3.07	3.00	0.62	0.31	7.00	10:10:2:1

Reaction condition: 10 wt% catalyst, MeOH to oil mole ratio of 9:1, and at 120°C



**Figure 4.11** The plot of methyl ester yield over ETS-10 (CS) versus reaction time.

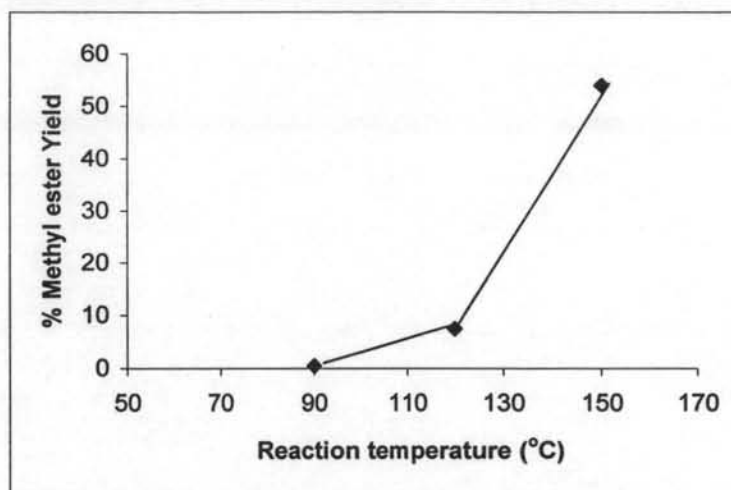
#### 4.2.5 Effect of reaction temperature

The catalytic activities of ETS-10 (CS) in the transesterification of palm oil at various reaction temperatures are shown in Table 4.8. The reaction temperatures were varied in the range of 90-150°C. The catalyst activity depends strongly on the reaction temperature. By increasing temperature from 90 to 120 and 150°C, methyl ester yield increases from 0.47 to 7.53 and 53.98 wt%, respectively. Methyl ester yield increases with increasing temperature. The optimum temperature is 120°C because the difference between catalytic and non-catalytic reaction are more pronounced at this temperature. At 150°C the methyl ester yield is up to 53.98 wt% but it was only 10.65 wt% higher than the thermal reaction without catalyst at the same temperature. That means that the increasing product yield is caused by thermal effect more than catalytic effect. The ETS-10 could not play an efficient role of catalyst at 150°C as good as the reaction carried out 120°C. The amount of glycerol also increases at 150°C.

**Table 4.8** The catalytic activities of ETS-10 (CS) in the transesterification of palm oil at various reaction temperatures

Reaction temperature (°C)	Methyl ester yield (wt%)				Total yield (wt%)	MO:MP:ML:MS wt ratio
	MO	MP	ML	MS		
90	0.20	0.21	0.04	0.02	0.47	10:11:2:1
120	3.50	3.12	0.61	0.30	7.53	11:10:2:1
150	24.83	20.80	5.93	2.42	53.98	8:7:2:1

Reaction condition: 10 wt% catalyst, MeOH to oil mole ratio of 9:1, and for 24 h



**Figure 4.12** The plot of methyl ester yield over ETS-10 (CS) versus reaction temperature.

In conclusion the optimized condition for transesterification of palm oil to biodiesel with ETS-10 catalyst was found to be 10 wt% catalyst to reactant mixture, methanol to palm of 9:1, at 120°C for 24 hours. This optimized condition was applied in further study with modified ETS-10 catalysts.

### 4.3 Catalytic activities of ETGeS-10 in transesterification reaction

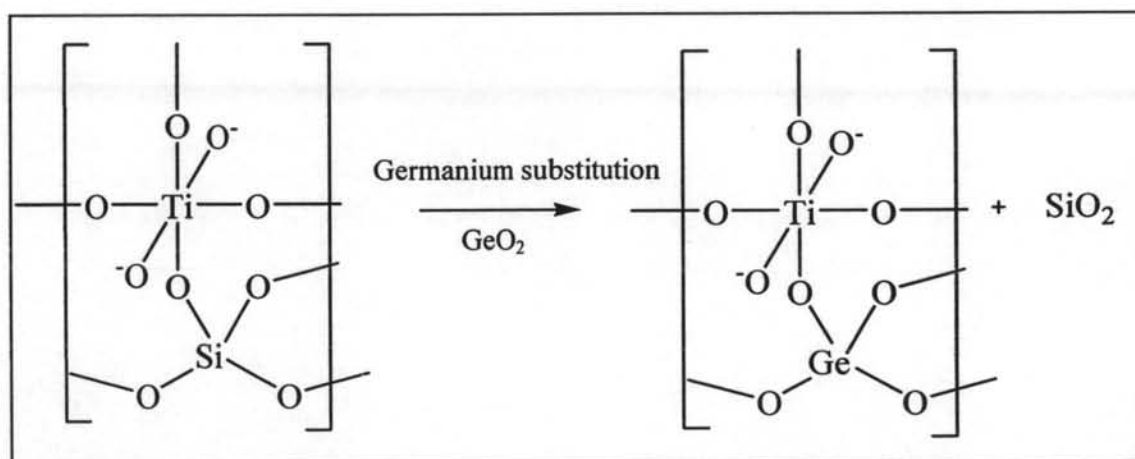
Table 4.9 shows the catalytic activities of ETGe<sub>x</sub>S-10 where x is 0.15 to 1.5 compared with ETS-10 having no germanium and pure GeO<sub>2</sub>. The methyl ester yield for pure GeO<sub>2</sub> is only 1.56 wt% which is quite low compared to other ETS-10 and ETGe<sub>x</sub>S-10 catalysts. At low germanium contents in ET(Ge)<sub>x</sub>S-10 catalysts (x = 0.15 and 0.5), methyl ester was produced at the yield of 3.22 and 13.30 wt%, respectively. A 2 times increased was found for ETGe<sub>x</sub>S-10 (x = 0.5) compared to ETS-10 (CS). According to the XRD result, both ETGe<sub>x</sub>S-10 catalysts still remain the structure of ETS-10. Thus the significant increase in activity is due to germanium atoms in the ETS-10 framework. The result is related to the increased basicity due to incorporated germanium in framework similar to what was observed for germanium-containing faujasite [65]. The proposed structure is depicted in Figure 4.13. When ET(Ge)<sub>x</sub>S-10 (x = 1.0) was used as catalyst, the activity still increases in spite of no ETS-10 structure found in its XRD pattern. This is not accounted by the new unidentified phase because the yield decreases when ET(Ge)<sub>x</sub>S-10 (x = 1.5) was used as catalyst. It

may be due to other phase such as quartz which was increased in amount with increasing the germanium loading.

**Table 4.9** The catalytic activities of ETGeS-10 catalysts in transesterification reaction of palm oil

Catalyst	Methyl ester yield (wt%)				Total yield (wt%)	MO:MP:ML:MS wt ratio
	MO	MP	ML	MS		
ETS-10 (CS)	3.50	3.12	0.61	0.30	7.53	11:10:2:1
ETGe <sub>x</sub> S-10						
x = 0.15	1.42	1.34	0.32	0.14	3.22	9:8:2:1
x = 0.5	6.06	5.50	1.16	0.58	13.30	10:9:2:1
x = 1.0	16.56	14.38	3.88	1.60	36.42	9:7:2:1
x = 1.5	10.43	9.52	2.25	1.00	23.20	9:8:2:1
GeO <sub>2</sub>	0.66	0.71	0.13	0.06	1.56	10:11:2:1

Reaction condition: 10 wt% catalyst, MeOH to oil mole ratio of 9:1, at 120°C, and for 24 h.



**Figure 4.13** Proposed structure of germanium substituted ETS-10.

#### 4.4 Catalytic activity of Na-loaded ETS-10 in transesterification reaction

The ETS-10 and Na-loaded ETS-10 materials are compared in their catalytic activities and the results are shown in Table 4.10. Na-modified methods in this research were ion-exchange to produce NaETS-10 and impregnation with NaOH and NaOAc to produce NaOH/ETS10 and NaOAc/ETS-10, respectively. Base-modified ETS-10 catalysts from both ion-exchange and impregnation methods provide higher methyl ester yield compared with ETS-10 (CS). Base-modified catalysts followed by calcination at 450°C could improve the catalytic activity compared with oven-dried sample due to the increase in occluded sodium oxide species and more space for reaction after the complete removal of moisture from cavities of the catalysts. The strength of basic site occurred via the decomposition of sodium compounds to form extra framework basic Na<sub>2</sub>O. NaOH/ETS-10 (C) exhibits 79.80 wt% yield which increases by 12.55% compared to NaOH/ETS-10 (D) whereas NaETS-10 (C) and NaOAc/ETS-10 (C) provide methyl ester yield increased by 13.15% and 19.54%, respectively, compared to the corresponding oven dried catalysts.

**Table 4.10** The catalytic activities of Na-loaded ETS-10 catalysts in transesterification reaction of palm oil

Catalyst	Methyl ester yield (wt%)				Total yield (wt%)	MO:MP:ML:MS wt ratio
	MO	MP	ML	MS		
ETS-10 (CS)	3.50	3.12	0.61	0.30	7.53	11:10:2:1
NaETS-10 (D)	28.93	26.50	6.33	2.66	64.42	9:8:2:1
NaETS-10 (C)	35.38	31.28	7.91	3.00	77.57	9:8:2:1
NaOH/ETS-10 (D)	32.89	24.26	6.95	3.14	67.25	9:7:2:1
NaOH/ETS-10 (C)	35.52	34.16	7.16	2.95	79.80	10:10:2:1
NaOAc/ETS-10 (D)	24.91	22.06	5.55	2.22	54.75	9:8:2:1
NaOAc/ETS-10 (C)	33.79	31.36	6.00	3.14	74.29	11:10:2:1

Reaction condition: 10 wt% catalyst, MeOH to oil mole ratio of 9:1, at 120°C, and for 24 h (D denoted for dried sample and C for calcined sample).

Considering the effects of Na sources and Na modified methods, NaOH impregnated ETS-10 (NaOH/ETS-10) exhibits the highest methyl ester yield of 79.80 wt% followed by Na-exchanged ETS-10 (NaETS-10) and NaOAc impregnated ETS-10 (NaOAc/ETS-10) catalysts at methyl ester yield of 77.57% and 74.29%, respectively. Methyl ester yield for NaETS-10 catalyst was close to that of NaOH/ETS-10. Nevertheless, the SEM image of NaOH/ETS-10 shows the remained sodium species that indicates the competitive homogeneous catalyst leaching from the ETS-10 to the reaction media during the catalysis course. Then NaETS-10 was chosen to improve the biodiesel yield and further study.

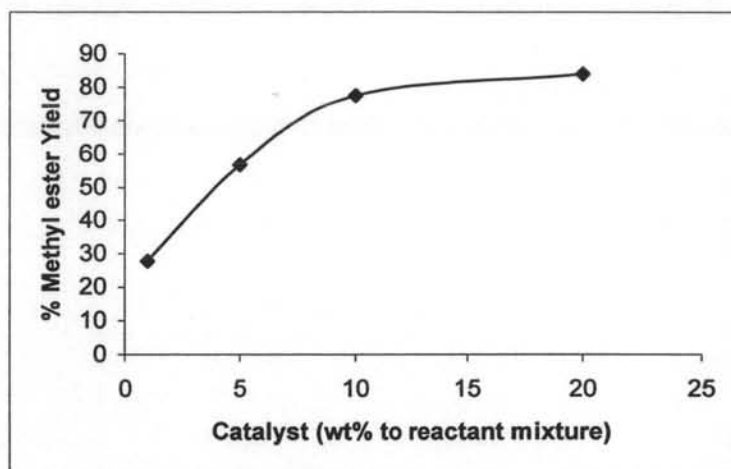
#### 4.4.1 Effect of NaETS-10 amount

The catalytic activities of NaETS-10 at various catalyst amounts of 1, 5, 10 and 20 wt% in the transesterification of palm oil are shown in Table 4.11 and the corresponding plot of methyl ester yield versus catalyst amount is shown in Figure 4.14. The drastically increased yield was obtained by increasing the catalysts amount from 1 to 10 wt%. The yield increased slowly when the catalyst amount was increased between 10 and 20%. According to the methyl ester yield, the catalysts amount of 10 % to reactant mixture was chosen for the rest of study for NaETS-10.

**Table 4.11** The catalytic activities of NaETS-10 at various catalyst amounts in the transesterification of palm oil

Catalyst wt%	Methyl ester yield (wt%)				Total yield (wt%)	MO:MP:ML:MS wt ratio
	MO	MP	ML	MS		
1	12.18	11.70	2.68	1.14	27.70	9:9:2:1
5	25.83	23.06	5.41	2.48	56.78	10:9:2:1
10	35.38	31.28	7.91	3.00	77.57	9:8:2:1
20	38.50	33.86	8.25	3.36	83.97	9:8:2:1

Reaction condition: NaETS-10 as catalyst, MeOH to oil mole ratio of 9:1, at 120°C, and for 24 h.



**Figure 4.14** The plot of methyl ester yield versus catalyst amount of NaETS-10.

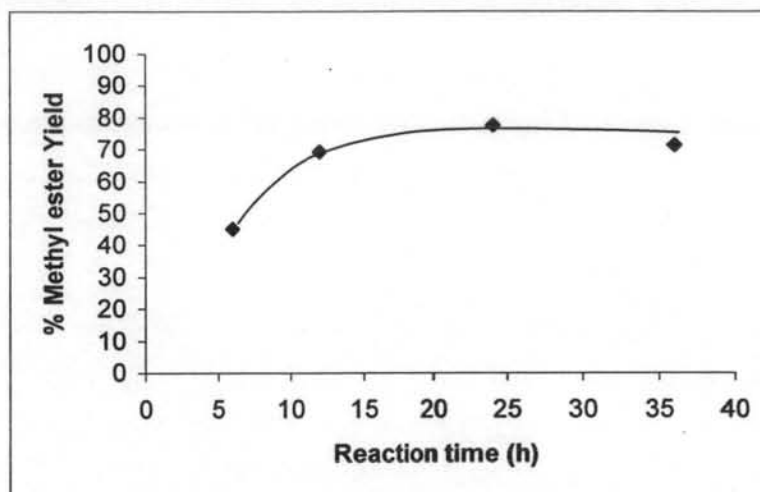
#### 4.4.2 Effect of reaction time

The catalytic activities of NaETS-10 in the transesterification of palm oil at different reaction time are shown in Table 4.12. The reaction time was varied in the range of 6-36 h. It is obvious that the reaction time of 6 h is not enough for the completion of the transesterification of palm oil over NaETS-10 at 120 °C. Extension of reaction time over 12 h is not necessary although the reaction time of 24 h can provide the highest ester yield. The reaction time between 12-36 h makes no big deal on the yield of methyl ester. There is no drastic difference in ester distribution by varying reaction time.

**Table 4.12** The catalytic activities of NaETS-10 in the transesterification of palm oil for different reaction time

Reaction time (h)	Methyl ester yield (wt%)				Total yield (wt%)	MO:MP:ML:MS wt ratio
	MO	MP	ML	MS		
6	20.43	18.02	4.86	1.80	45.11	8:7:2:1
12	32.06	27.15	6.89	3.08	69.18	9:8:2:1
24	35.38	31.28	7.91	3.00	77.57	9:8:2:1

Reaction condition: 10 wt% catalyst, MeOH to oil mole ratio of 9:1, and at 120°C.



**Figure 4.15** The plot of methyl ester yield over NaETS-10 versus reaction time.

#### 4.4.3 Effect of reaction temperature

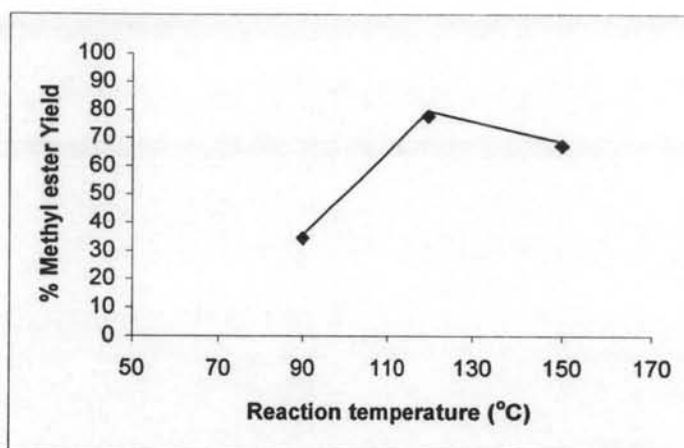
The catalytic activities of NaETS-10 in the transesterification of palm oil at various reaction temperatures from 90 to 150°C are shown in Table 4.13. The plot looks much different from that for ETS-10 without Na loading. By increasing temperature from 90 to 120, methyl ester yield increases from 34.30 to 77.57 wt%. A decline of ester yield to 67.12 wt% was found when the temperature was increased to 150°C. That might be caused by the basic active site was changed to deactivated site when temperature was increased. The optimum temperature is thus 120°C. High temperature had no effect to increase the methyl ester yield when NaETS-10 was used compared with ETS-10. All three cases provide much higher ester yield than the thermal reaction without catalysts.

**Table 4.13** The catalytic activities of NaETS-10 in the transesterification of palm oil at various reaction temperatures

Reaction temperature (°C)	Methyl ester yield (wt%)				Total yield (wt%)	MO:MP:ML:MS wt ratio
	MO	MP	ML	MS		
90	15.30	14.31	3.27	1.42	34.30	9:9:2:1
120	35.38	31.28	7.91	3.00	77.57	9:8:2:1
150	30.93	27.09	6.07	3.03	67.12	10:9:2:1

Reaction condition: 10 wt% catalyst, MeOH to oil mole ratio of 9:1, and for 24 h





**Figure 4.16** The plot of methyl ester yield over NaETS-10 versus reaction temperature.

#### 4.4.4 Activities of regenerated and Na-reloaded catalysts

It is well known that the outstanding advantage of heterogeneous catalyst is ease of separation and reuse. In this research, the used catalyst was regenerated by washing with acetone, drying and calcination prior to the retest for its activity. The catalytic activities of regenerated Na-loaded catalysts in the transesterification of palm oil are shown in Table 4.14. When the regenerated catalysts of NaETS-10 and NaOH/ETS-10 were used, the ester yields decrease by 32.70% and 16.75%, respectively, and especially in NaOAc/ETS-10, methyl ester yield was extremely decreased by 48.11%. The loss in activities of catalysts may be from the deactivation of active sites. In addition, the decrease in activities may not a result from Na leaching out because of the difference between Na/Ti before and after reaction is less than 0.1.

#### 4.4.4.1 Effect of regenerated catalysts

**Table 4.14** The catalytic activities of regenerated Na-loaded catalysts in the transesterification of palm oil

Regenerated catalyst	Methyl ester yield (wt%)				Total yield (wt%)	MO:MP:ML:MS wt ratio
	MO	MP	ML	MS		
NaETS-10	20.97	16.97	4.85	2.08	44.87	9:7:2:1
NaOH/ETS-10	29.55	24.47	6.34	2.69	63.05	9:8:2:1
NaOAc/ETS-10	12.23	10.00	2.75	1.20	26.18	9:7:2:1

Reaction condition: 10 wt% catalyst to reactant mixture, MeOH to oil mole ratio of 9:1, at 120°C, and for 24 h

#### 4.4.4.2 Effect of Na-reloaded catalysts

However, the regenerated catalysts can be improved their activities when the calcined used catalyst was reloaded with NaOH by either ion exchange or impregnation and the results of regenerated catalysts were shown in Table 4.15. The methyl ester yields were improved from 63.05% for regenerated catalyst to 73.73% for Na-reloaded NaOH/ETS-10 catalysts, almost the same as the fresh catalyst. For NaETS-10, the catalyst reloaded by ion exchange also gain its activity back even in the third run to give the yield very close to that using the fresh catalyst.

**Table 4.15** The catalytic activities of Na-reloaded catalyst in the transesterification of palm oil

Na-reloaded catalyst	Methyl ester yield (wt%)				Total yield (wt%)	MO:MP:ML:MS wt ratio
	MO	MP	ML	MS		
NaOH/ETS-10	34.45	27.97	7.92	3.39	73.73	9:7:2:1
NaETS-10 (1 <sup>st</sup> )	34.35	31.09	7.80	2.96	76.20	9:8:2:1
NaETS-10 (2 <sup>nd</sup> )	34.53	31.19	7.31	2.86	75.89	9:9:2:1

Reaction condition: 10 wt% catalyst, MeOH to oil mole ratio of 9:1, at 120°C, and for 24 h

A summary of methyl ester yield over various catalysts evaluated in this study are concluded in Figure 4.17. At the optimum conditions, Na-modified exhibits the highest methyl ester yield in the order of NaOH/ETS-10  $\approx$  NaETS-10 > NaOAc/ETS-10 > ETGeS-10, ETS-10 (CS) and ETS-10 (WG), respectively. The basicity of catalyst was the most significant factor to reach the high methyl ester yield and other parameters such as catalyst amount, starting material for catalyst preparation, molar ratio, reaction time and reaction temperature also affect the yield of methyl ester or biodiesel.

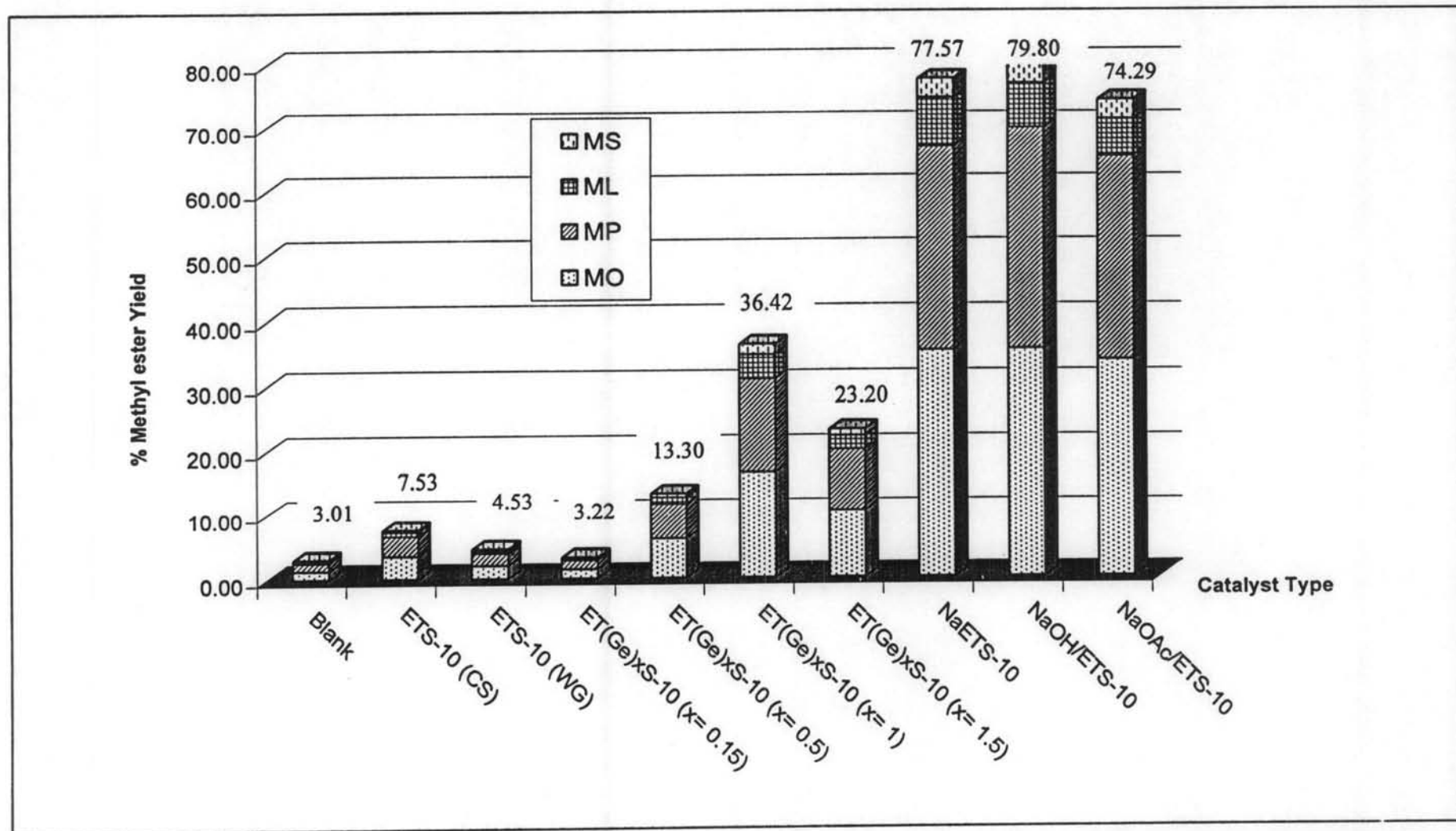


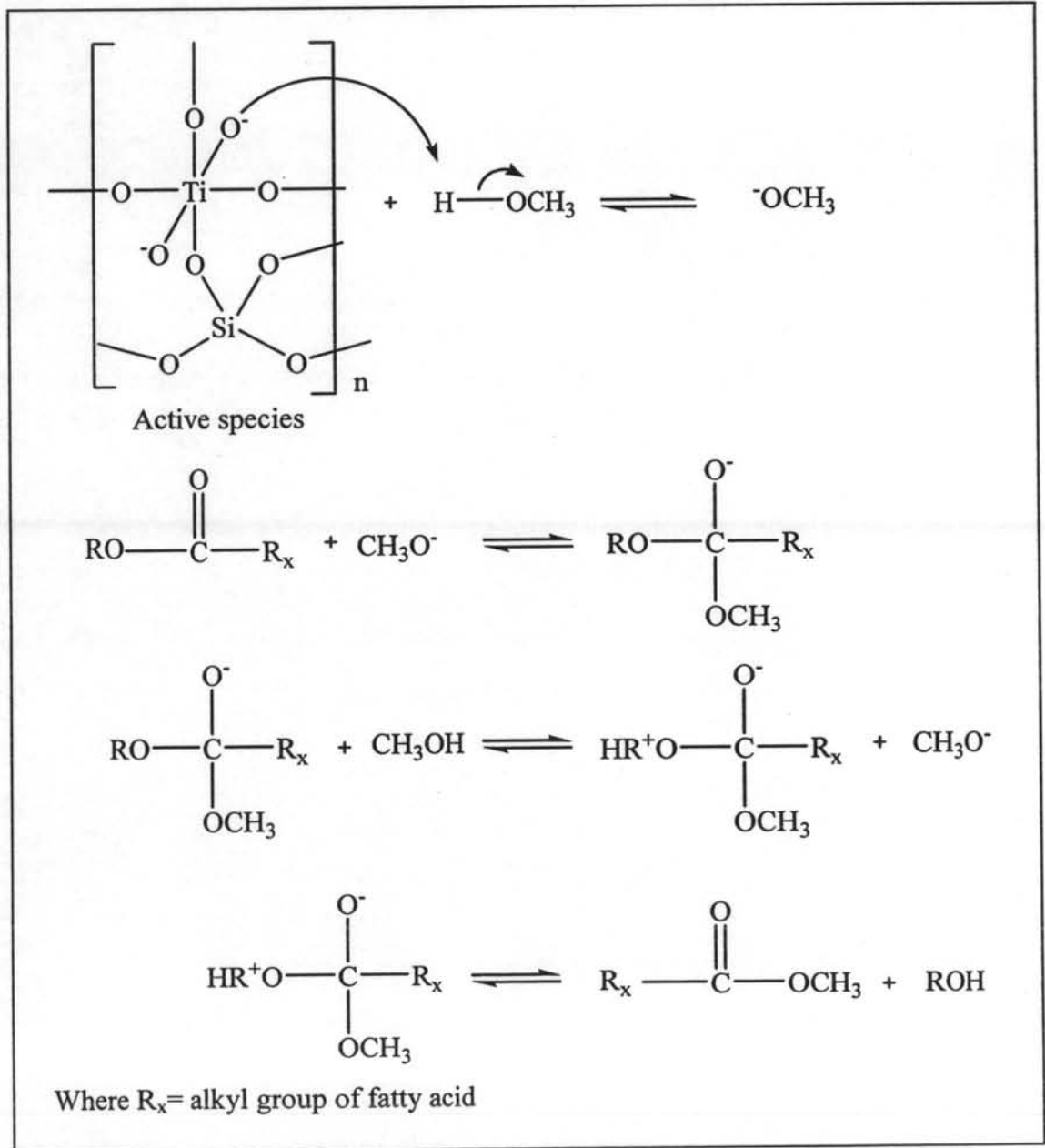
Figure 4.17

Methyl ester yield from transesterification reaction of palm oil over calcined catalysts, 10 wt% catalyst, MeOH to oil mole ratio of 9:1, at 120°C, and for 24 h.

## 4.5 Proposed transesterification mechanism

### 4.5.1 Transesterification mechanism for ETS-10

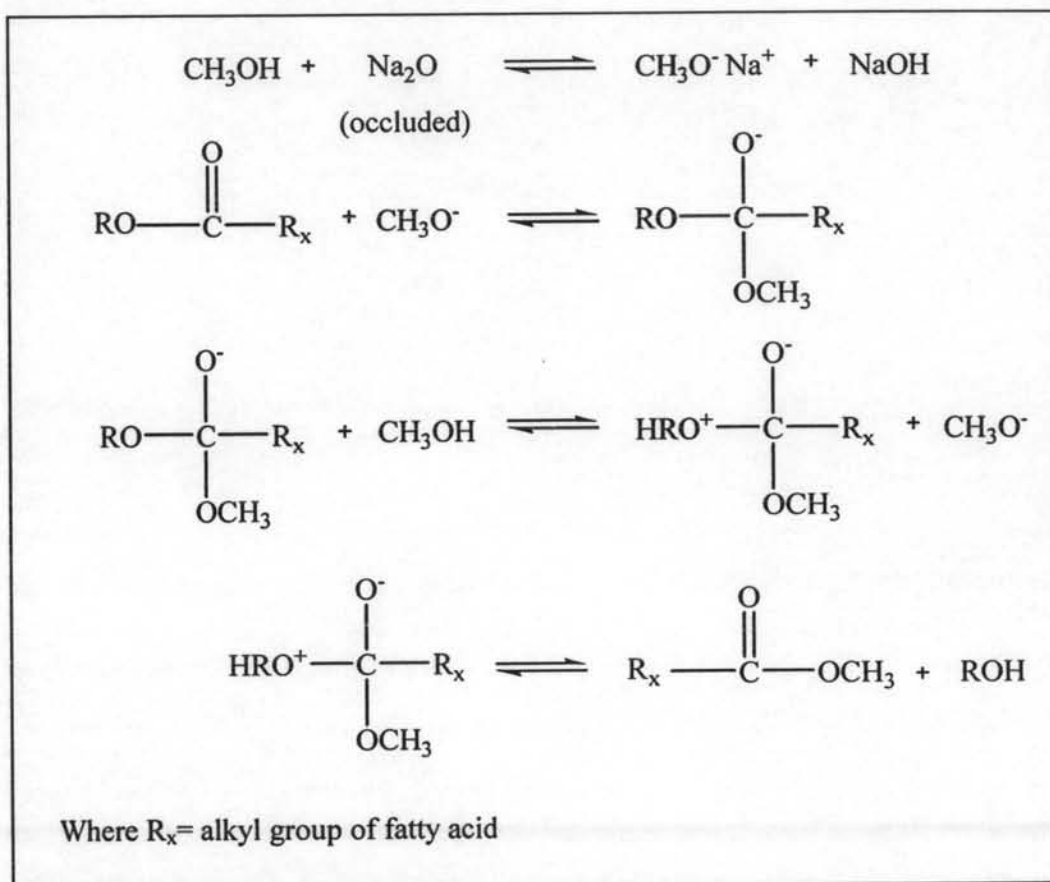
ETS-10 structure is composed of  $\text{TiO}_6$  octahedral and  $\text{SiO}_4$  tetrahedral link through the oxygen atom. The framework carrier two negative charges and the electrical balance were preserved by extra-framework cations. The mechanism was started from a framework octahedral Ti atom reacting with methanol to generate methoxide ion. Then this active species further react with triglyceride to produce methyl esters as shown in Figure 4.18.



**Figure 4.18** Proposed transesterification mechanism for ETS-10.

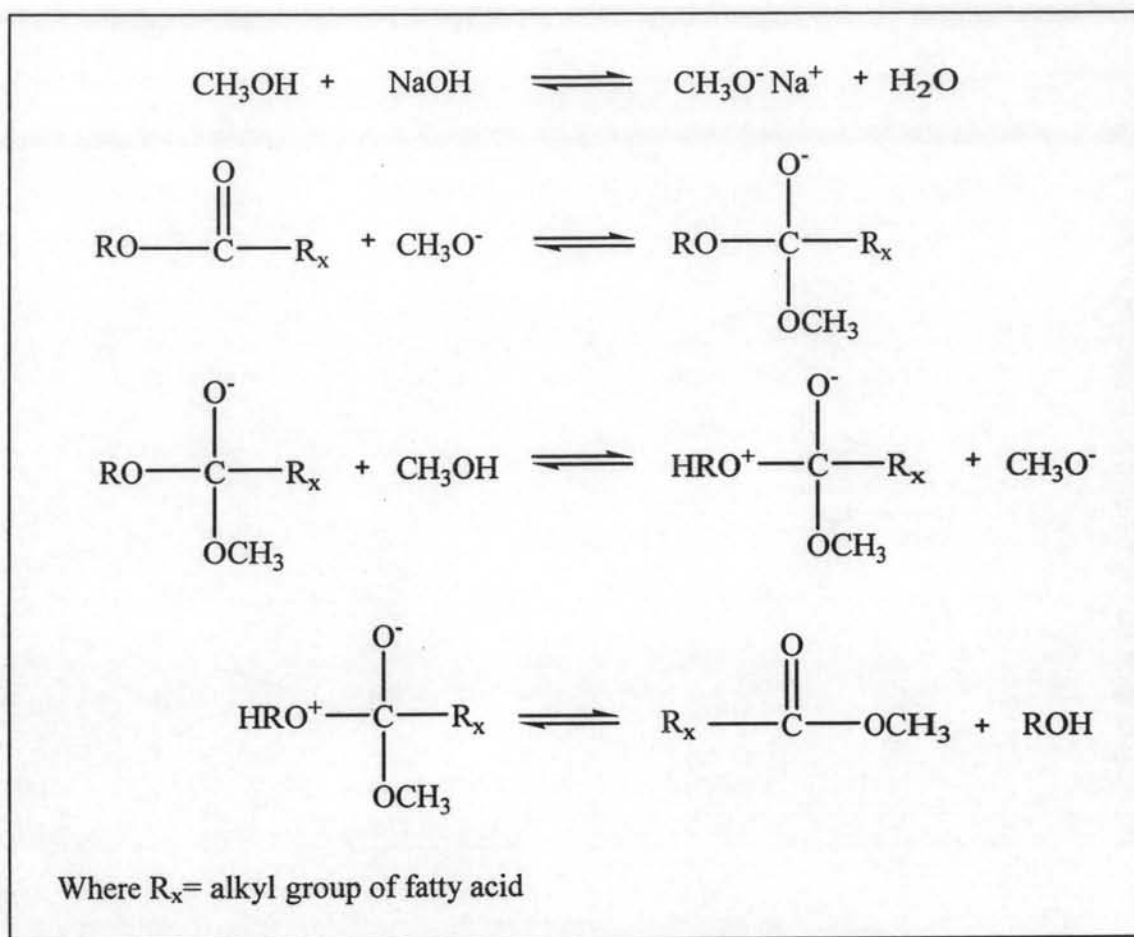
#### 4.5.2 Proposed mechanism for Na-loaded ETS-10

The mechanism for Na-loaded ETS-10 is believed to consist of two parts, one is octahedral Ti species behaving as in ETS-10 without Na loading that mentioned in 4.2.1 and the other is occluded sodium oxide species as shown in Figure 4.19.



**Figure 4.19** Proposed transesterification mechanism for occluded sodium oxide in Na-loaded ETS-10.

Moreover, NaOH generated during the reaction pathway also reacts with methanol to generate the active methoxide ions which further reacts with triglyceride to produce more methyl esters product as explained in Figure 4.20.



**Figure 4.20** Proposed transesterification mechanism for sodium hydroxide species.