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Stearic Acid Esters Synthesized using Iron Exchanged Montmorillonite K10 Clay Catalysts

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***Abstract*— In this study the effects of reaction parameters for production of stearic acid esters catalyzed by cation exchanged montmorillonite K10 (MMT K10) were studied. Iron exchanged MMT K10 (Fe-MMT K10) with four different concentrations of Fe^{3+} (0.25 M, 0.5 M, 0.75 and 1 M) catalysts were used to catalyze the esterification reaction of stearic acid with two alcohols i.e. ethanol and methanol. The catalysts were prepared via cation exchanged method and characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM) equipped with energy dispersive x-ray (EDX), thermal gravimetric analysis (TGA), and the acidity of catalysts was measured using pyridine adsorption technique monitored by FTIR spectroscopy. The effects of various reaction parameters such as catalysts concentration, reaction time and type of alcohol have been investigated. High stearic acid conversion reached up to 75% for reaction conducted with methanol at 80 ºC was obtained when 0.75 M and 1 M Fe-MMT K10 were used as the catalysts. This suggests that the cation exchanged MMT K10 can be a potential catalyst for industrial applications.**

Keyword; Cation exchanged, Montmorillonite K10, Esterification, Stearic acid.

I. INTRODUCTION

Esters have a significant role in the industrial applications such as, fragrance, adhesive, pharmaceutical, cosmetics, food additives and lubricants [1,2]. Esterification of fatty acids with short chain alcohols is very important as this can contribute to the production of biodiesel. Biodiesel, derived from renewable oils or fats, is alkyl esters of long-chain fatty acid, has become the focus of international attention as a source of energy. This is due to the fact that it is environmentally friendly, non-toxic, biodegradable, reduces the emission of carbon dioxide in the atmosphere and emits pollutants less than normal diesel [3, 4]. The esterification reaction normally carried out using homogeneous Brønsted acid catalysts such as sulfuric acid, but using such catalyst has some difficulties such as the corrosion of equipment, waste generation and environmental problems [5].

The use of heterogeneous catalysts in the esterification reaction provides catalysts that can be re-used and also reduced waste generation. Varieties of heterogeneous catalysts have been used in esterification of long chain acid. Sulphated zirconia has been studied in the esterification of oleic acid [6], zirconia-modified silica in esterification of oleic acid with trimethylolpropane [7], raw halloysite as a catalyst for esterification of lauric acid [8], and MMT clays i.e. KSF, KSF/0, KP10, and K10 in synthesis of fatty acid esters from stearic, oleic, and palmitic acids with short-chain alcohols [1].

The emphasis on environmental protection, as industrial and economic growth gave birth to many forms of pollution threatening human health and earth ecosystems, resulted in the growth of environmental catalysis. Recently, focus has been centered on the use of clay minerals as heterogeneous catalysts due to their properties; low coast, easily available, as well as environmental friendly. Montmorillonite (MMT K10) the major clay mineral commercially available has been used as a heterogeneous catalyst for many applications [9]. There are considerable methods which can be used to modify MMT to improve its catalytic properties, such of these methods include cation exchange which considered as efficient catalysts that due to it reusability without losing its activity, also increasing the strength of Lewis acid site [10]. Cation-exchanged MMT (Al^{3+}, Fe^{3+}, Cr^{3+}, Zn^{2+}, Cu^{2+}, Ni^{2+}) have been used as catalysts in esterification of succinic acid with iso-butanol, with conversion higher than 90% after 8 hours [11].

Our team focuses on the use of cation-exchanged MMT K10 as catalyst for esterification of stearic acid as to date there is no work has been done on using cation-exchanged MMT for esterification of long chain acid. This work aims to understand the parameters that affect the conversion of fatty acids when it is reacted with short chain alcohols is essential to obtain the better results.

II. MATERIALS AND METHODS

A. Fe- MMT K10 Preparation

A series of Fe- MMT clays catalysts were prepared by adding 10 g of MMT K10 to 0.25, 0.5, 0.75, 1 M aqueous solution of $Fe(NO_3)_3$ at 80 ºC for 8 h. Then the slurry was cooled, filtered and washed thoroughly with distilled water. The samples were dried at room temperature, then at 100 °C for 12 hours, followed by calcination at 300 °C for 4 hours [10,12].

B. *Catalyst Characterization*

X-ray diffraction (XRD) was obtained by using Bruker AXS Germany diffractometer model D8 Advance, Cu-Kα, (λ =1.5418Å) at 40 kV and 40 mA. The patterns were collected over the range of 5ºC to 50ºC for 2θ at room temperature. Scanning electron microscopy (SEM) images were obtained by Hitachi SU 1510 and energy dispersive X-ray spectroscopy (EDX) data was obtained by Horiba EMAX, operated at 15 kV. The acidity of catalysts was measured using pyridine adsorption followed by FTIR spectroscopy using a Varian equipment model 3100 using KBr technique. The thermal effect and extent of weight loss in temperature range 20 ºC to 1000 ºC were monitored using N_2 gas via thermogravimetric analysis (TGA) BP model RB-3000.

C. *Reaction Procedure*

The esterification reactions of stearic acid with ethanol and methanol were carried out at 80 ºC for 3 hours with 2 g of stearic acid in 100 ml of alcohols and 600 mg of solid catalysts [2]. The percentage of conversion of stearic acid to ester was determined by titration with 0.02 M NaOH.

III. RESULT AND DISCUSSION

A. *X-Ray Diffraction*

XRD of unmodified and modified MMT K10 are shown in Fig. 1. X-ray patterns reveal that the modified samples have structural characteristics nearly identical to the unmodified MMT K10. The basal spacing of d001 was observed for all samples at ca. 10.01 Å (peak at 2θ ≈ 8.8°) which indicates the presence of 2:1 (T:O:T) structure [2]. The remarkable similarities between the diffragtograms of the samples indicate that clay structure is retained during the exchanged processes.

This refers to the interlayer clay was not affected by Fe^{3+} exchanged reaction. This is consistent with what has been studied by Fang et al. [13] where they suggested that metal cations were fixed solely on the outer surfaces of the clay. Any inclusion of metal cations in the interlayer of clay would increase the d values. Fatima et al. [14] points out that the aluminum pillared MMT showed a shift of d001 reflection towards lower 2θ, which resulted in the increasing of d001 value. They proposed that the Al_2O_3 was inserted in the interlayer of clay.

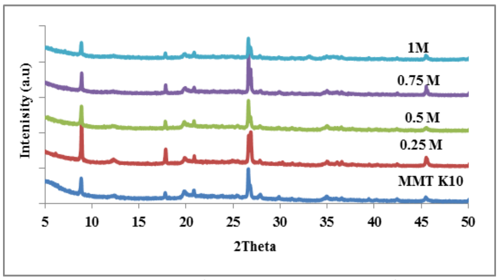


Fig. 1: XRD patterns of MMT K10 and modified samples

B. *SEM/EDX*

SEM images of MMT K10 and modified samples are shown in Fig. 2 while the elements composition (%) from EDX analysis is given in Table I. According to SEM images, the crystalline nature of the iron exchanged clay is maintained and this has also been detected in the XRD result that no change in the interlayer spacing occur during the cation exchange process. It can be clearly seen that the clay surface after exchanged process has non-aggregated morphology and there is a number of small flakes in the modified samples. From the EDX data, all samples show six elements, i.e. oxygen (O), iron (Fe), magnesium (Mg), aluminium (Al), silicon (Si), and potassium (K). These elements represent the components of MMT K10. The atomic percentage of Fe increased from 0.60% in MMT K10 to 5.31% in 1 M Fe-MMT K10 and this proves that the metal cation is largely distributed in the modified MMT K10 clay.

TABLE I. Elemental compositions (%) from EDX analysis of MMT K10 and modified samples.

MMT K10	O	F	Al	Si	K	Mg
Unmodified	67.49	0.60	4.70	25.79	0.57	0.85
0.25 M Fe	67.56	1.35	4.53	25.28	0.81	0.46
0.5 M Fe	67.84	2.07	4.21	24.95	0.42	0.51
0.75 M Fe	67.53	3.18	3.80	24.52	0.39	0.58
1M Fe	65.03	5.31	4.18	24.28	0.65	0.55

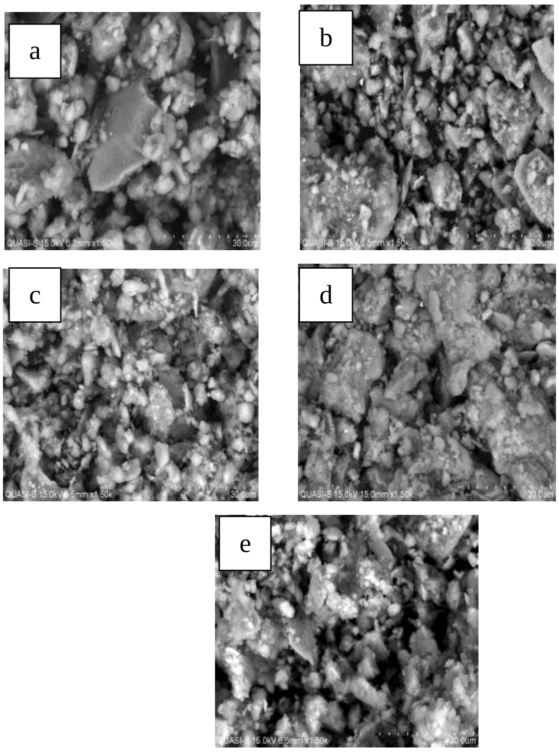
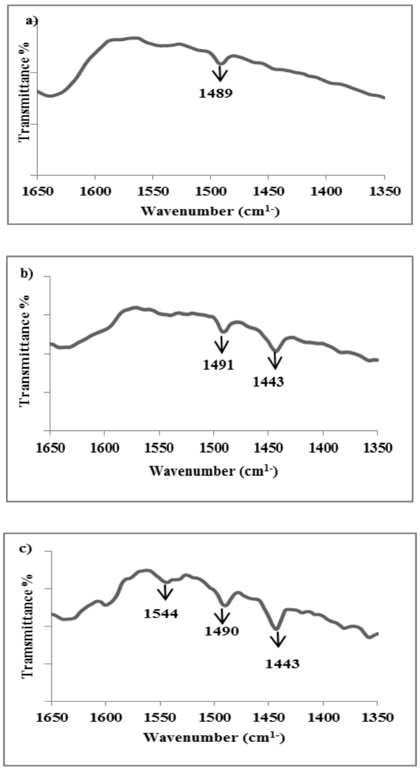


Fig. 2: SEM images of a) MMT K10, b) 0.25 M Fe-MMT K10, c) 0.5 M Fe-MMT K10, d) 0.75 M Fe-MMT K10, and e) 1 M Fe-MMT K10

C. *Acidity of Catalysts*

Fig. 3 shows the pyridine FTIR spectrum of unmodified and modified MMT K10 samples in the region 1350 to 1650 cm^{-1}. FTIR spectra show the vibration band at 1442, 1450 and 1489 cm^{-1} is related to Lewis acid site. While the bands at 1546 and 1639 cm^{-1} is related to Brønsted acid sites. The peak assignment was done based on previous work [11, 14, 15]. Fe-MMT K10 show bands at~1546 and 1639 cm^{-1} due to Brønsted acid sites, and band at ~ 1442 cm^{-1} due to Lewis acid sites, however the band at 1489 cm^{-1} due to both the Brønsted and Lewis acid sites, the intensity of this band slightly increase in modified samples. The Lewis acid sites in modified samples were increased with increasing in catalysts concentration as compared to unmodified MMT K10. This due to the ability of this guest cation in the MMT K10 to polarize the water molecules, which in the coordination sphere and accept pair of electrons from the nitrogen atom of the pyridine molecule. Thus the metal cation can potentially act as Lewis acid catalysts. Research conducted by Shimizu et al. [16] reported that the Lewis acid sites can be increased by changing the exchangeable cation by high hydration enthalpy metal cations.



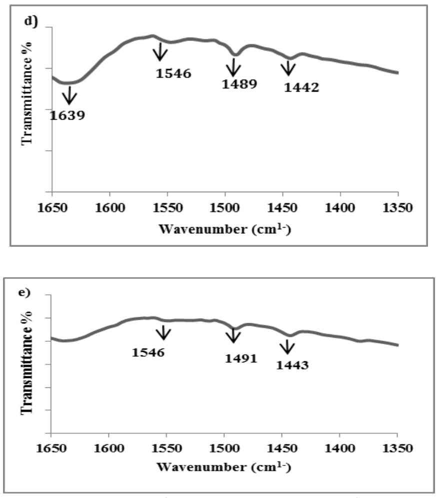


Fig 3: FTIR pyridine spectra of MMT K10 and modified samples where a) MMT K10, b)0.25 M Fe-MMT K10, c) 0.5 M Fe-MMT K10, d) 0.75 M Fe-MMT K10, and e) 1 M Fe-MMT K10

D. *Thermal Analysis*

TGA was conducted to determine the effect of the Fe modification on the thermal stability of the MMT K10 clay. Fig. 4 shows TGA curve of unmodified MMT K10 and as there is no significant difference in the weight loss trend between unmodified and Fe modified MMT K10, the other samples are not shown here. All samples have two mass loss steps, in the range from 20-1000 ºC; the thermal transition steps of the examined samples are demonstrated in Table II. The first step in the range from 40-290 ºC is related to the desorption of water molecules bounded to the exchangeable cations in interlayer space [7,17]. While the second step ca. between 280 ºC and 1000 ºC can be assigned to the dehydroxylation of –OH groups of MMT K10 clay [18,19]. After that the weight of the samples remained almost constant in further undergone to thermal treatment. From table II, it can be seen that an increase in the temperature was observed in modified samples due to the stronger hydrogen bonding between water molecules and Fe^{3+} [19]. The modified samples showed a lower wt % H_2O loss compared to unmodified MMT-K10, this indicates the modified samples have a better hydrophobic nature.

TABLE II. TGA results of MMT K10 and modified samples

MMT K10	**Step 1**		**Step 2**	
	Mass loss %	Temp ºC	Mass loss %	Temp ºC
Unmodified	14	39-284	4	285-987
0.25 M Fe	7.69	45-264	4	263-979
0.5 M Fe	7.38	37-299	3	298-973
0.75 M Fe	8.20	37-299	3	299-982
1 M Fe	8.58	36-310	3	311-986

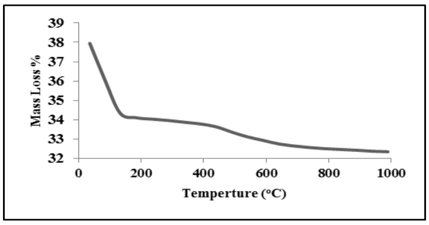


Fig 4: TGA curve of unmodified MMT K10

E. Esterification Reaction

1) Effect of Catalysts

The reactions were studied using unmodified and modified MMT K10 catalysts, while fixing the other conditions. The esterification of stearic acid with ethanol using catalysts at 80 °C is shown in Fig. 5a. It can be observed that the reaction occurred in the absence of catalyst and unmodified MMT K10 only gave 31 and 37 % acid conversion respectively. From the figure it can be seen clearly that the modified samples gave the highest acid conversion of up to 65 % compared to unmodified MMT K10. The increase in Fe^{3+} ion concentration affected the percentage of conversion and increased until 0.75 M Fe-MMT K10 then slightly decreased at 1M Fe-MMT K10. Eesterification of stearic acid with methanol at 80 °C is shown in Fig. 5b.

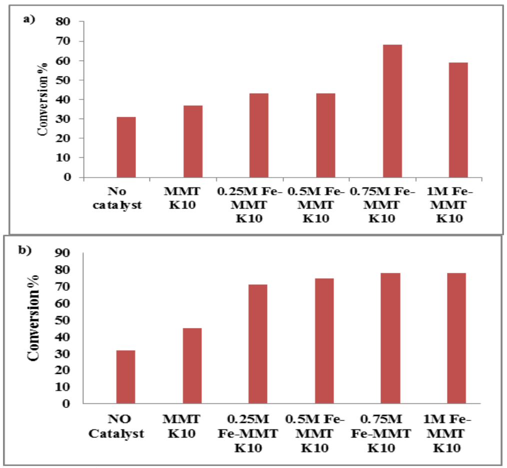


Fig 5: Effect of Fe^{3+} concentration on esterification of stearic acid at 80 °C after 3hours a) with ethanol and b) with methanol

The modified catalysts resulted in high acid conversion with increasing of cation exchanged concentration for up to 70 % for 0.75 and 1 M Fe-MMT K10 catalysts. Whereas the acid conversion without catalysts and with unmodified MMT K10 were 32 and 45 % respectively. For both type of alcohols used, Fe-MMT K10 samples were able to give higher stearic acid conversion compared to the esterification without catalyst and unmodified MMT K10. This is due to the fact that the Lewis acid sites were found to be increase in the modified samples as shown in the pyridine adsorption results. The effect of Fe^{3+} concentration is less than those types of alcohol and the reaction time. The presence of the catalysts in the esterification reaction is more important than the actual amount or concentration of it presents. That due to the esterification reaction slow reaction can give small acid conversion in the absence of catalyst [20].

2) Effect of Alcohol

The effect of alcohols used on stearic acid conversion at reaction temperature of 80 °C, for 3 h over montmorillonite K10 catalysts can be evaluated from fig. 6. Higher stearic acid conversion with methanol with all modified catalysts around 70% compared to reaction with ethanol was obtained in this study. The higher acid conversion using methanol has been reported in previous works. Study conducted by Aranda et al.[21] and Bassan et al. [22] conclude that this can be ascribed to the shorter chain length of methanol and its high polarity. The high conversion using methanol was also obtained in the esterification of oleic acid over Amazon flint kaolin [23], in this study used methanol 62.5 %, ethanol 27.3 % and 1-propanol 19.4 %. The authors have presented two reasons for this; the first one is depend on alcohol nucleophilicity, suggest that the large number of carbon atoms, lead to the lowest the alcohol nucleophilicity. The second reason is the alcohol length chain, when the alcohol length chain becomes larger; the approaching to the catalyst becomes more difficult. While Neji et al. [1] evaluated different alcohols i.e. methanol, ethanol, propanol and butanol in the esterification of stearic acid catalyzed by montmorillonite KSF/0 at 150 °C for 4 hours using semi-continuous reactor working above the boiling point of water and alcohol. This enable to continuous removal of the water produced which caused a shift in equilibrium towards the esterification. In their study butanol has higher boiling point 117.5 °C which evaporated at 150 °C at lower rate than the other alcohols, gave the higher acid conversion 99 %.

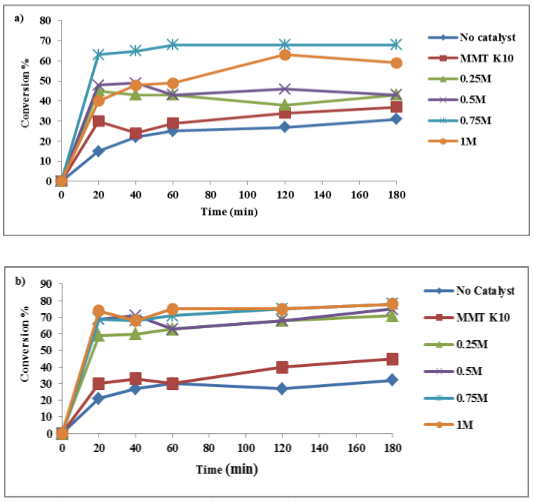


Fig 6: Effect of alcohol on esterification of stearic acid at 80 °C a) with ethanol and b) with methanol

3) Effect of Reaction Time

Fig. 7 shows the reaction time profile for the esterification reaction of stearic acid with ethanol and stearic acid with methanol catalysed by 0.75 M Fe-MMT K10 at 80 ºC. This catalyst was chosen as it gave the highest stearic acid conversion with ethanol and methanol compared to the other modified MMT K10 catalysts. The conversion of stearic acid increased with increasing reaction time. From the first 5 minutes of the reaction time, the conversion percentage with ethanol was 47 % after that the reaction proceed rapidly within 40 minutes 65%. Then, the conversion percentage remained almost constant until 180 minutes 68 %. For methyl stearate, the conversion percentage showed a different profile whereas the reaction achieved equilibrium from the first 5 minutes with percentage 68 %. Then the conversion percentage showed increase with increasing reaction time to show high value at 180 minutes 78 %. This due to the methanol properties as mentioned previously. For both type of alcohols used the acid conversion proceed very fast up to period of 60 minutes and then almost constant conversion until 180 minutes.In esterification reactions is expected the gradual increase of acid conversion with increasing in reaction time [23].

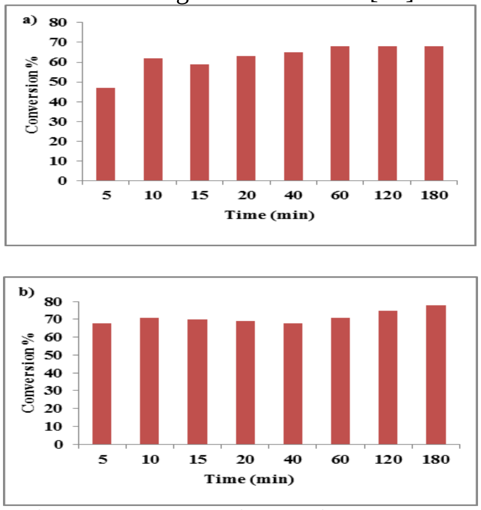


Fig 7: Effect of reaction time on esterification of stearic acid at 80 ºC and 0.75 M Fe-MMT K10 catalyst

IV. CONCLUSION

Three parameters have been chosen to optimize the synthesis of stearic acid esters; reaction time, catalysts concentration and type of alcohol. Higher acid conversion with ethanol obtained at reaction time 180 minutes and catalyst concentration 0.75M was 68%. While the higher acid conversion with methanol at same reaction conditions was 78%. This work suggests that the stearic acid esters can be synthesized at high acid percentage using catalysts prepared from simple and natural clay modified with the earth mineral i.e. Fe. Furthermore, it requires relatively low temperature i.e. 80 ºC and only a short time to achieve maximum conversion. This with the advantages hold by the clay such as present in abundance, low cost, as well as eco-friendly, and modification of clay only requires simple step, the use of clay as catalyst for many of organic synthesis.

Acknowledgment

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