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Esterification of Oleic Acid with Alcohols over Cu-MMT K10 and Fe-MMT K10 as Acid Catalysts

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Abstract. The esterification of free fatty acids with alcohols using montmorillonite (MMT) clay as heterogeneous catalyst is one of the methods to produce fatty acid alkyl ester that can be used as alternative renewable biofuels. However, the unmodified MMT gives low conversion of free fatty due to the limitation of acid sites in the clay structure. This work focuses on preparation of an environmental friendly catalyst from montmorillonite K10 (MMT K10) clay catalyst for the esterification of oleic acid with various alcohols. Esterification of oleic acid with alcohols has been carried out in the presence of metal exchanged MMT K10 (M-MMT K10; M = Fe^{3+} and Cu^{2+}). The concentrations of both Fe^{3+} and Cu^{2+} precursors were varied at 1 M and 4 M. The effect of different alcohols used, molar ratio of reactants and catalyst loading on the esterification reaction was investigated. Among the exchanged clay catalysts, 4 M Fe-MMT K10 was found to be more active for the esterification of oleic acid with methanol. The maximum oleic acid conversion (ca. 68.5%) was achieved after 3 hours of reaction at the reaction temperature of 60 °C with molar ratio of methanol to oleic acid of 10:1 and catalyst loading of 5 wt% relative to the mass of oleic acid. The catalytic activity was found to be directly related to the amount of cation used in the modification step and Brønsted acidity of metal exchanged MMT K10 clay catalyst.

INTRODUCTION

The esterification of free fatty acids (FFA) with alcohols using heterogeneous catalyst is one of the methods to produce fatty acid alkyl esters that can be used as alternative renewable biodiesels in industry. Biodiesels are essentially required since the demand for petroleum fuels are escalating and with diminishing availability of fuels and energy source nowadays. Biodiesels produced from vegetable oils or animal fats have similar properties and performances to the conventional diesel fuels, thus, make it one of the popular possible alternative to overcome the increasing price of petroleum also with environment concerns [1].

It was proven that acid catalyst can be used in the esterification of FFA for the production of biodiesel from high FFA oil content [2]. Homogeneous acid catalysts such as H_2SO_4, HF, H_3PO_4, HCl and p-toluene sulfonic acid have been used in the esterification of FFA [2, 3]. However, the use of this type of catalyst requires neutralization and separation steps to the process in addition to the esterification reaction [4]. This in turns increase the cost of biodiesels production.

The use of clay minerals as heterogeneous catalysts for chemical reactions is an exciting component of green chemistry. Montmorillonite K10 (MMT K10) is a low-cost clay mineral that has been used widely as a heterogeneous acid catalyst in various type of organic synthesis such as epoxidation [5], hydrogenation [6] and hydroxyalkylation [7]. MMT K10 has received subsequent attention due to its favorable characteristics such as low cost, high selectivity, large surface area, mechanical and thermal stability, reusability and also environmental compatibility [8].

MMT is a layered aluminosilicates clay mineral that can be classified as 2:1 type dioctahedral smectites. Silica tetrahedral (Si^{4+} coordinated with O^{2-}) and alumina octahedral (Al^{3+} coordinated with O^{2-}) are interconnected by the

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sharing of O^{2-} at polyhedral corners and edges. That made up of an octahedral (O) sheet of Al sandwiched between two tetrahedral (T) silica sheets thus making the composition of T-O-T. The space between each sheet is called the interlayer spacing containing exchangeable cations. Many forms of substitutions in the structure are possible to occur in the octahedral and tetrahedral positions. This can leave it with a negative charge which is balanced by exchangeable positive charge cations such as Al^{3+}, Fe^{3+}, Cu^{2+} and Zn^{3+} [9–12].

Cation exchanged MMT has been used for esterification of short to medium chain carboxylic acids such as succinic acid [13], propionic acid [14], ethanoic acid, butanoic acid, hexanoic acid, octanoic acid and decanoic acid [15]. The production of fatty acid ester from steric acid using untreated MMT K10 as catalyst has been reported previously [16]. However, the conversion of stearic acid obtained was less than 60% even though the reaction was conducted at high temperature (150 ºC) for 5 hours of reaction time. A work has been previously reported on the catalytic activity of cation exchange MMT K10 for esterification of stearic acid and it was proven that this type of MMT modification can improve the stearic acid conversion of up to 78% with a relatively low temperature i.e. 80 ºC and a short time to achieve maximum conversion [17]. Optimization of esterification reaction using response surface methodology (RSM) based on 3-variable of Box-Behnken design (BB) has proven that 1 M Cu-MMT K10 was able to covert 87.05% of stearic acid at 80 ºC within 60 minutes [18].

In this work, MMT K10 was modified with Fe^{3+} and Cu^{2+} at various concentrations and the resulting materials were characterized with regard to the changes in their acidity and textural properties. To optimize the oleic acid conversion, certain reaction parameters were varied such as type of alcohol, molar ratio of reactants and mass of catalyst.

MATERIALS AND METHOD

Modification and Characterization of M-MMT K10

M-MMT K10 clays were modified by slurring 10 g MMT K10 powder in 50 ml of aqueous solutions of iron (III) chloride ($FeCl_3$) and copper (II) chloride ($CuCl_2$) at two different concentrations i.e. 1 M and 4 M. The mixtures were stirred 90 ºC for 8 hours. The slurry was then cooled, filtered and washed thoroughly with distilled water. The presence of chloride was tested using $AgNO_3$ solution. The solids formed were dried at 100 ºC for 12 hours then calcined in the furnace at 300 ºC for 4 hours [19].

Energy dispersive X-ray spectroscopy analysis (EDX) (Horiba EMAX model EX 250) was used to determine the amount of Fe and Cu in the MMT K10. Brunauer-Emmett-Teller (BET) surface area, pore volume and pore size distribution were obtained from N_2-adsorption-desorption isotherms at 77.3 K measured by Quantachrome gas sorption analyzer, model Micromeritic ASAP 2020 surface area analyzer. The distribution of Brønsted and Lewis acid sites on the surface was measured using the pyridine adsorption followed by the FTIR analysis. The solid catalyst ca. 0.5 g was dried in an oven for 1 hour at 100 ºC, then 0.1 cm^3 of pyridine was exposed to the samples overnight. The samples were redried at 120 ºC for one hour to remove the physisorbed pyridine [14]. The Brønsted and Lewis acids were determined by FTIR using the KBr pellet. The FTIR analyses of the catalysts were carried out in the range of 1650 – 1350 cm^{-1} using the Varian equipment model 3100.

Catalytic Activity of M-MMT K10

In this section, the effect of alcohol carbon chain (methanol, ethanol, *n*-propanol and *n*-butanol), molar ratio of alcohol:oleic acid (10:1, 20:1 and 30:1) and mass of catalyst (5 wt% and 7 wt%) were investigated. The appropriate amounts of oleic acid, alcohol and catalyst were added to a 250 cm^3 round-bottomed flask fitted with a reflux condenser. The esterification reaction was allowed to proceed for 3 hours whilst stirring vigorously at 60 ºC [20]. The percentage of oleic acid conversion was determined by titration with 0.02 M NaOH. The samples were taken from the reactor at every 15 minutes for the first 1 hour, and every subsequent hour for 3 hours.

The conversion of the oleic acid was calculated using the following formula [16]:

$$\text{Percentage of conversion (\%)} = \text{X acid} = (ai\text{-}at)/ai \times 100$$

where (ai) is the initial acidity of oleic acid mixture at t_0 and (at) is the acidity of oleic acid mixture at (t) time.

RESULTS AND DISCUSSION

Catalyst Characterization

Surface Area Analysis

As can be seen in Table 1, there is not much variation in the specific surface area of the Fe modified samples as compared to the unmodified MMT K10 sample. However, higher surface area of Cu-MMT K10 samples in comparison to that of unmodified MMT K10 and Fe-MMT K10 samples (Table 1) suggests that the Cu modified samples may have lower amount of the trapped pores which can be explained by the emergence of micropores (<20 Å) as a result of the arrangement of Cu^{2+} in the interlayer spacing of this sample [21].

It was reported that apart from the cation exchange process that occurs at planar sites, Cu^{2+} is found to be located inside the interlayer of MMT K10 through the interaction with the aluminosilicate sheets [22]. This contributes to the increment in the surface area of Cu-MMT K10 samples as the micropores produced in the interlayer spaces [23].

TABLE 1. Surface areas of unmodified, Fe and Cu modified MMT K10

Sample	Surface area (m^2/g)
MMT K10	202.0
1 M Fe-MMT K10	205.0
4 M Fe-MMT K10	202.0
1 M Cu-MMT K10	222.0
4 M Cu-MMT K10	217.0

Energy Dispersive X-ray Spectroscopy (EDX)

The atomic compositions (%) of Al, Fe and Cu from EDX analysis are given in Table 2. The elements of Al and Fe represent the component of MMT K10 and thus these elements were detected in all modified samples. While the element of Cu in unmodified sample was not detected due to its absence in the raw sample [24]. The EDX analysis revealed that the Fe and Cu contents in the prepared samples are in accordance with varied Fe and Cu contents in the exchange process. The higher concentration of Fe^{3+} and Cu^{2+} solutions produced a higher Fe and Cu percentages in the modified MMT K10. EDX data of Fe^{3+} and Cu^{2+} exchanged montmorillonite show a depletion of some aluminium upon exchange with these cations [13]. An increment in atomic compositions of 4 M Cu-MMT K10 and 4 M Fe-MMT K10 can be attributed to the higher concentration of metal cations applied in exchange process that form compact packing of metallic particles in the interlamellar layer of catalyst [25].

TABLE 2. Composition of elements (%) from EDX analysis of unmodified, Fe and Cu modified MMT K10

Sample	Al	Fe	Cu
MMT K10	5.73±0.8	2.18±0.7	n.d.
1 M Fe-MMT K10	4.13±0.8	6.00±1.1	n.d.
4 M Fe-MMT K10	3.71±0.4	10.53±2.2	n.d.
1 M Cu-MMT K10	4.43±0.5	1.32±0.4	0.64±0.6
4 M Cu-MMT K10	4.11±0.2	1.49±0.2	1.20±0.2

(n.d.: not detected)

Surface Acidity

The IR spectra in the spectral region between 1350 and 1650 cm^{-1} after pyridine treatment followed by thermal desorption at 120°C for 1 hour are represented in Fig. 1. Clearly the MMT K10 sample has the Brønsted acid sites with the presence of peaks labelled as B (ca. 1490 cm^{-1}, 1548 cm^{-1} and 1635 cm^{-1}). The 1540 cm^{-1} band is typical of this site that can be attributed to the pyridinium ion (PyH^+) [26]. The presence of pyridine interaction with Lewis acid sites (L) can be assigned to the bands at ca. 1450 cm^{-1}, 1490 cm^{-1} and 1610 cm^{-1}. After metal cations modification, these peaks were found to increase in their peak intensities indicating that the Brønsted and Lewis acidity have been improved with the insertion of metal cations. The presence of Fe^{3+} and Cu^{2+} ions in the clay structure has influenced the acidity of the clay surface. High charge and small size of Fe^{3+} ion increased the intensity of Brønsted/Lewis acid peaks while the divalent Cu^{2+} ion produced low intensity of the acid peaks. It can be clearly

seen that the peak intensities of Brønsted/Lewis acid sites for the spectrum of 4 M Fe-MMT K10 have increased significantly as compared to the other samples. The increase of acidity of 4 M Fe-MMT K10 was probably due to the polarization of the interlayer hydration sphere with small size and highly-charged metal cations [27].

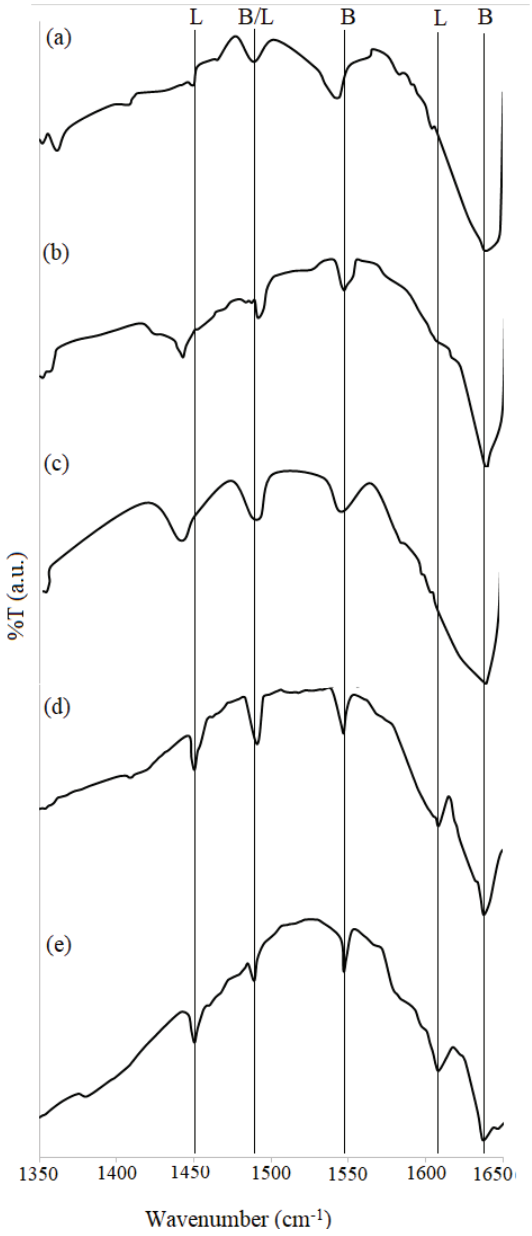

FIGURE 1. FTIR spectra of pyridine adsorption on a) unmodified MMT K10, b) 1 M Fe-MMT K10, c) 4 M Fe-MMT K10, d) 1 M Cu-MMT K10 and e) 4 M Cu-MMT K10

Catalytic Activity

Effects of Catalysts

To investigate the catalytic activity of the modified MMT K10 catalysts, the esterification of oleic acid was initially carried out in methanol under reflux and the reaction conditions were optimized to obtain the optimum oleic acid conversion. The results of this study are shown in Fig. 2.

It is evidenced from the conversion of oleic acid to methyl oleate that all catalysts tested have catalytic activity under the conditions used in this work. However, the modified MMT K10 samples clearly showed significant increment in conversion of oleic acid as compared to the unmodified MMT K10 sample. It can be seen that surface area had no correlation with the catalytic activity of the catalysts. Cu modified MMT K10 samples with slightly higher surface area than Fe MMT K10 samples gave lower conversion of oleic acid. This was previously been observed in the esterification of stearic acid [16] and benzylation of benzene [28] using commercial clays.

The amount of Fe^{3+} in the MMT K10 structure gives significant impact on the oleic acid conversion. 1 M Fe-MMT K10 with ca. 6.00% atomic mass of Fe relative to other elements present in the clay structure converted ca. 60% of oleic acid as compared to 4 M Fe-MMT K10 with ca. 10.53% of Fe converted ca. 70% of oleic acid. This can be associated to the improvement in Brønsted acidity of 4 M Fe-MMT K10 sample arising by the exchange of interlayer hydrated cation by Fe^{3+} ions. Brønsted acid sites act as the active sites that present in the interlamellar water molecules on the edge sites which coordinated to the exchangeable ions. This Brønsted acid sites initiate the esterification reaction by protonating the oleic acid and promote the esterification reaction with methanol [13]. It is clear that the role of Fe^{3+} content and acidity are more significant than surface area of MMT K10.

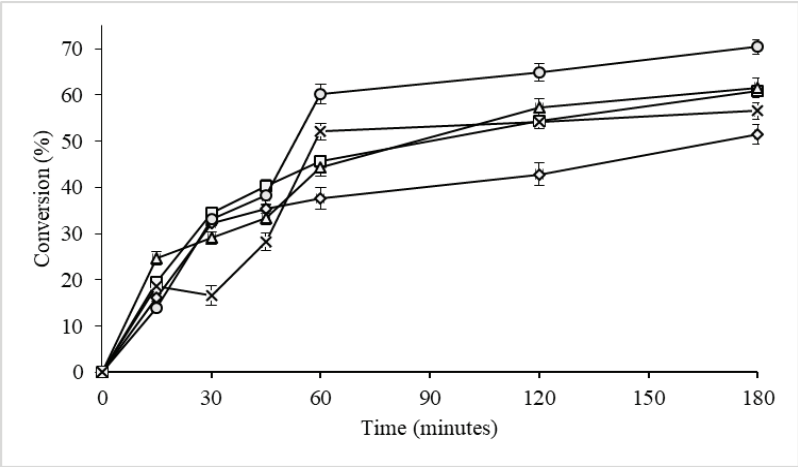

FIGURE 2. Effect of catalyst on the esterification of oleic acid with methanol. Reaction conditions: methanol and oleic acid molar ratio 10:1, temperature = 60 ºC and 5% w/w of mass catalyst over mass of oleic acid. ◊ = MMT K10, Δ = 1 M Fe-MMT K10, o = 4 M Fe-MMT K10, × = 1 M Cu-MMT K10 and □ = 4 M Cu-MMT K10

Effects of Alcohols

In order to optimize the oleic acid conversion, the factor of length of alcohol carbon chain used was investigated. The same reaction parameters were used for this investigation. The 4 M Fe-MMT K10 was chosen as the catalyst as it gave the maximum conversion of oleic acid. As can be clearly seen in Fig. 3, methanol with the shortest carbon chain gave the highest conversion of oleic acid relative to ethanol, *n*-propanol and *n*-butanol. This could possibly due to the optimum activation energy has been achieved when methanol was used under the reaction temperature of 60 ºC. Therefore, in order to reduce intermolecular associations of ethanol, *n*-propanol and *n*-butanol for dispersed adsorption and to avoid clustering of alcohols around the Brønsted acid sites by hydrogen bonding, the activation energy is required by increasing the reaction temperature [29].

It was also suggested that the conversion of acid obtained in the esterification with alcohol depends on the alcohol nucleophilicity where the longer carbon chain length leads to the less nucleophilicity of alcohol, hence reduce the ability to donate an electron pair [30]. Steric effect also plays an important factor in determining the oleic acid conversion. As the size of alcohol hydrocarbon chain increases, the steric hindered access of the alcohol to the electrophilic site of oleic acid [31].

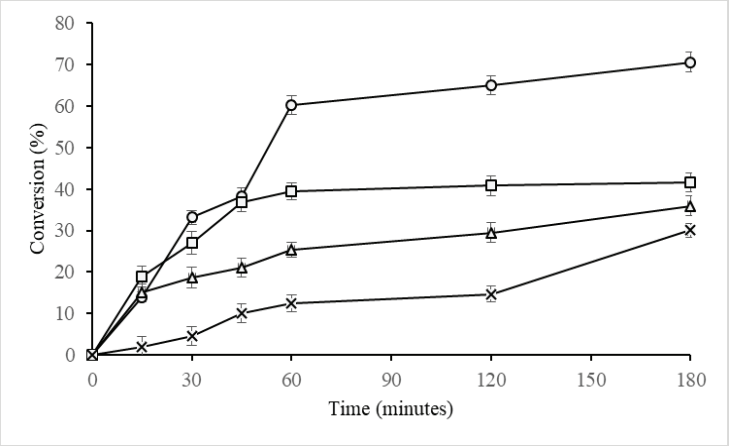

FIGURE 3. Effect of alcohol on the esterification of oleic acid. Reaction conditions: catalyst = 4 M Fe-MMT K10; alcohol and oleic acid molar ratio 10:1, temperature = 60 ºC and 5% w/w of mass catalyst over mass of oleic acid. o = methanol, □ = ethanol; Δ = *n*-propanol; × = *n*-butanol

Effects of Reactants Molar Ratio

To study the effect of molar ratio of alcohol to oleic acid on the catalytic activity of modified MMT K10, the reaction was carried out with methanol catalyzed by 4 M Fe-MMT K10 and the catalyst amount was fixed as 5 wt% at 60 ºC. From Fig. 4, it is obvious that 10:1 molar ratio of methanol to oleic acid converted the maximum amount of oleic acid. Meanwhile, molar ratio of 20:1 and 50:1 can only convert ca. 40% of oleic acid. This implies that an increase in the alcohol concentration impedes the esterification reaction that could be due to the blocking of active sites on the catalyst. This was previously observed in the esterification of lauric acid using halloysite as catalyst [32]. The blockage of active sites on catalyst surface may hindered the protonation of oleic acid which lead to the less conversion [1].

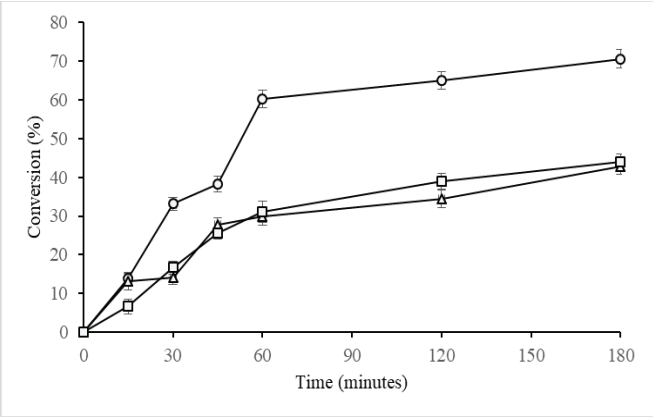

FIGURE 4. Effect of methanol to oleic acid molar ratio on the esterification of oleic acid. Reaction conditions: catalyst = 4 M Fe-MMT K10; temperature = 60 ºC and 5% w/w of mass catalyst over mass of oleic acid. o = 10:1, □ = 20:1; Δ = 50:1

Effects of Mass of Catalyst

The amount of 4 M Fe-MMT K10 catalyst was varied between 5 wt% and 7 wt% relative to the mass of oleic acid while keeping the molar ratio of methanol:oleic acid at 10:1. The reaction was carried out at 60 ºC for 3 hours. Catalyst loading of 5 wt% showed slightly higher conversion compared to 7 wt% (Fig. 5). It should be noted that for the first 60 minutes of reaction time, 7 wt% of catalyst gave faster reaction rate in comparison to 5 wt%. This can be associated to the increase of catalytic active sites of the catalyst participated in the reaction [33]. However, as the

reaction proceeded in longer time, the conversion values remain unchanged indicates that the reaction has achieved its equilibrium condition.

On the contrary, esterification of oleic acid with addition of 5 wt% of 4 M Fe-MMT K10 produce a maximum amount of oleic acid conversion. The gradual increase of oleic acid conversion to methyl ester by decreasing the mass of catalyst shows that the equilibrium has not been reached. This could be probably due to the low viscosity of the reaction medium which increases the interaction between the catalyst and reaction components [34]. Therefore, the maximum conversion of acid can be obtained with low amount of catalyst.

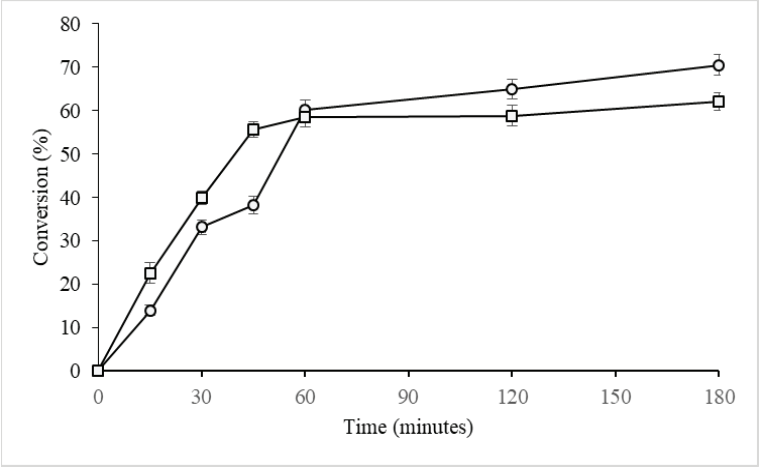

FIGURE 5. Effect of mass of catalyst on the esterification of oleic acid with methanol. Reaction conditions: catalyst = 4 M Fe-MMT K10; temperature = 60 ºC and molar ratio of methanol to oleic acid = 10:1 5% w/w of mass catalyst over mass of oleic acid. o = 5% w/w, □ = 7% w/w

CONCLUSIONS

The esterification of oleic with short chain alcohols over cations modified MMT K10 was efficiently carried out in a reflux system at low reaction temperature (60 ºC). 4 M Fe-MMT K10 has proven to be the most effective catalyst among the tested catalysts as it has the improved Brønsted acid sites content in its clay structure as compared to the unmodified and Cu-MMT K10 catalysts. The results showed that esterification reaction achieved ca. 70% of oleic acid conversion at optimum reaction conditions in 3 hours reaction time (methanol as the source of alcohol, a molar ratio of methanol to oleic acid of 10:1 in the presence of 5 wt% catalyst), Therefore, iron modified MMT K10 is a promising catalyst for biodiesel production as it required a relatively low temperature i.e. 60 ºC and only a short time to achieve maximum conversion.

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