

## Metal cation exchanged montmorillonite K10 (MMT K10): Surface properties and catalytic activity

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**Abstract:** Al-MMT K10, Fe-MMT K10 and Cu-MMT K10 were prepared via cation exchanged method. The modified MMT K10 catalysts were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM) equipped with energy dispersive x-ray (EDX), N<sub>2</sub>-sorption at 77.3 K, the acidity of catalysts was measured using pyridine adsorption method followed by Fourier transform infrared (FTIR) spectroscopy and thermal stability using thermal gravimetric analysis (TGA). Structural investigation of modified samples by XRD and SEM revealed that the basic structure of clay is retained during the exchanged processes. N<sub>2</sub>-adsorption isotherms showed that all samples are of Type IV with hysteresis loop type H3 according to Brunauer, Emmett and Teller (BET) classification, and the modified samples decreased in the surface area. Pyridine adsorption analysis exhibited that the Lewis acid sites in all modified samples were increased as compared to the unmodified. The catalysts were evaluated for the esterification of stearic acid with methanol. Higher conversions were achieved in a short time and at relatively mild reaction temperature using modified MMT K10 relative to raw MMT K10. This suggests that the cation exchanged MMT K10 can be a potential catalyst for industrial applications.

**Key words:** Cation-exchange; Montmorillonite K10; Esterification; Stearic acid; Methanol

### 1. Introduction

Clay minerals have been widely used as heterogeneous catalysts for many types of organic synthesis, due to their favorable properties such as low cost, thermal stability, selectivity, large surface area, easily separated as well as environmental friendly (Zatta et al., 2013). Montmorillonite (MMT) clay has been used further than the other types of clay mineral. It is a layered aluminosilicates clay mineral that can be classified as 2:1 type dioctahedral smectites, with its crystalline structure consists of multiple layers and each layer made up of one octahedral alumina sheet sandwiched between two tetrahedral silica sheets. The interlamellar water layers in clay contain dissolved cations sandwiched between extended aluminosilicate sheets (Jha et al., 2013; Tyagi et al., 2006). Cations present in the interlayer parent clay can be exchanged with high charge density cations like Al<sup>3+</sup> and Fe<sup>3+</sup> and thus acidity can be imparted in the clay. This property makes MMT as a suitable heterogeneous catalyst for many chemical reactions (Jha et al., 2013; Joseph et al., 2005; Aher et al., 2012; Reddy et al., 2004).

Esterification reaction requires mineral acid such as sulphuric acid as a homogeneous catalyst, which may constitute a risk to the environment (Binitha et al., 2011). So there have been extensive studies to develop a method that is eco-friendly technique to produce the esters. It was resorting to use solid

acids as heterogeneous catalysts in esterification reaction, such as ion exchange resins (Kuzminska et al., 2015; Kitakawa et al., 2015), zeolites (Milina et al., 2014; Purova et al., 2015), sulphated oxides (Kaur et al., 2015), and clay catalysts (Igbokwe and Olebunne, 2011; Reddy et al., 2005; Bhorodwaj and Dutta, 2011; Dharne and Bokade, 2011). Esterification of fatty acids with short chain alcohols is very important as this can contribute to production of bio-diesel. 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 (Thanh et al., 2012; Upadhyay et al., 2013). Different types of heterogeneous catalysts have been used in esterification of long chain acid. Sulphated zirconia has been studied in esterification of oleic acid (Misi et al., 2010), zirconia-modified silica in esterification of oleic acid with trimethylolpropane (Kuzminska et al., 2014), raw halloysite as a catalyst for esterification of lauric acid (Zatta et al., 2011), 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 (Neji et al., 2009).

Montmorillonite; the major clay mineral commercially available can be modified to improve its properties. There are considerable methods which can be used to modify MMT. Such of

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these methods include cation exchange, pillaring and acid activation. Cation exchanged MMT K10 is considered as efficient catalysts since it can be re-used several times without losing its activity, also increasing the strength of Lewis acid site (Aher et al., 2012). A study conducted by Joseph et al., (2005) used  $\text{Cu}^{2+}$ -MMT K10 as a catalyst for direct addition of N-H bond to CC triple bond. This  $\text{Cu}^{2+}$  exchanged MMT K10 showed increasing in Lewis acidity and gave high activity at higher reaction temperatures. Reddy et al., 2007 studied the surface acidity of  $\text{M}^{n+}$ -MMT ( $\text{M}^{n+} = \text{Al}^{3+}, \text{Fe}^{3+}, \text{Cr}^{3+}, \text{Zn}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}$  and  $\text{H}^+$ ) and their catalytic activity toward esterification of succinic acid with *iso*-butanol. The trivalent cations exchanged have strong Brønsted acidity and highest ester yield 96%, whereas the divalent cation exchanged showed strong Lewis acidity and lowest esters yield 27%.

To the best of our knowledge, the use of cation exchanged MMT K10 as catalyst in the esterification of fatty acids has not yet been investigated. Thus, this work focuses on the procedure for synthesis, characterization and the catalytic activity of cation exchanged MMT K10 towards the esterification of stearic acid with methanol.

## 2. Materials and method

### 2.1. Catalyst preparation

Cation exchanged MMT K10 ( $\text{M}^{n+}$ -MMT K10) clays were prepared by adding 10 g of MMT K10 to 0.75 M aqueous solutions of  $\text{Cu}(\text{CO}_2\text{CH}_3)_2 \cdot \text{H}_2\text{O}$ ,  $\text{AlCl}_3$  and  $\text{Fe}(\text{NO}_3)_3$  to obtain Cu-MMT K10, Al-MMT K10 and Fe-MMT K10 respectively at 80 °C 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 (Aher et al., 2012; Darehkjordi et al., 2012).

### 2.2. Catalyst characterization

X-ray diffraction (XRD) pattern was obtained by using Bruker AXS Germany diffractometer model D8 Advance, Cu-K $\alpha$ , ( $\lambda = 1.5418 \text{ \AA}$ ) at 40 kV and 40 mA. The patterns were collected over the range of 5 $\theta$  to 50 $\theta$  for 2 $\theta$  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. Brunauer-Emmett-Teller (BET) surface area, pore volume and pore size distribution were obtained from  $\text{N}_2$ -adsorption-desorption isotherms at 77.3 K measured by Quantachrome Instruments. The acidity of catalysts was measured using pyridine adsorption method measured by FTIR spectroscopy of Varian equipment model 3100 using KBr technique. The thermal effect and extent of weight loss in temperature range 20 °C to 1000 °C were monitored using  $\text{N}_2$  gas via thermogravimetric analysis (TGA) BP model RB-3000.

## 2.3. Catalytic activity

The catalytic activity of the catalyst was measured via esterification of stearic acid with methanol. The reactions were carried out at 80 °C for 3 hours with 2g of stearic acid in 100 ml of methanol and 600 mg of solid catalysts (Dharne and Bokade, 2011). The percentage of conversion of stearic acid to ester was determined by titration with 0.02 M NaOH.

## 3. Result and discussion

### 3.1. X-Ray diffraction

XRD of unmodified MMT K10 and modified samples 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  $2\theta \approx 8.8^\circ$ ) which indicate the presence of 2:1 (T:O:T) structure (Dharne and Bokade, 2011). The remarkable similarities between the diffractograms of the samples indicate that clay structure is retained during the exchanged processes. This refers to the interlayer clay was not affected by  $\text{M}^{n+}$  exchanged reaction. This is consistent with what has been studied by Fang et al. (2014) 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. (2011) points out that the aluminum pillared MMT (PILM) showed a shift of d001 reflection toward a lower  $2\theta$ , which resulted in the increase in d001 value. This suggested that the  $\text{Al}_2\text{O}_3$  was intercalated in the interlayer of clay.

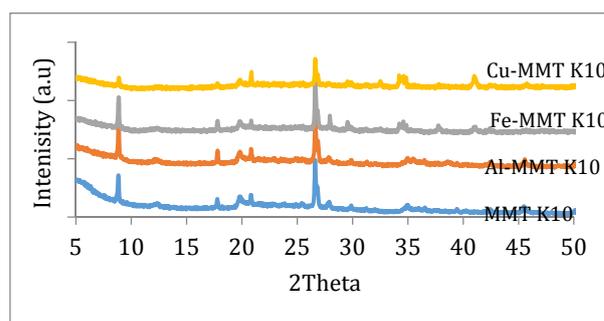


Fig. 1: XRD patterns of MMT K10 and modified samples

### 3.2. SEM/EDX

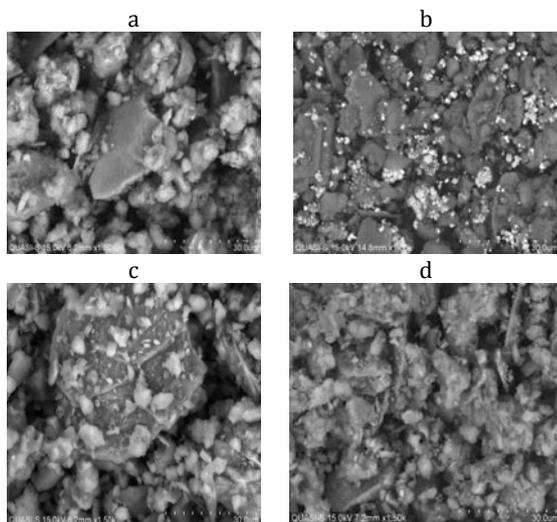
SEM images of MMT K10 and modified samples are shown in Fig. 2 while the cations composition (%) from EDX analysis is given in Table 1. According to SEM images, the crystalline nature of the cation exchanged clay is maintained and this has also been detected in the XRD results. It can be clearly seen that the clay surface after exchanged process has non-aggregated morphology and there is a number of small flakes in the modified samples (Dutta et al., 2011; Siboni et al., 2015).

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 element of Cu in unmodified MMT K10 was not detected but clearly from the SEM image, the shiny parts were observed for Cu-MMT K10 and EDX

data reveals that 8.87% of Cu was detected. Meanwhile, the atomic percentage of Fe and Al were increased from 0.57 and 4.46% in MMT K10 to 3.18 and 6.30% in Fe-MMT K10 and Al-MMT K10 respectively.

**Table 1:** Atomic percentage of Fe, Al and Cu in modified MMT K10

Fe %		Al %		Cu %	
MMT K10	Fe- MMT K10	MMT K10	Al- MMT K10	MMT K10	Cu- MMT K10
0.57	3.18	4.46	6.30	-	8.87



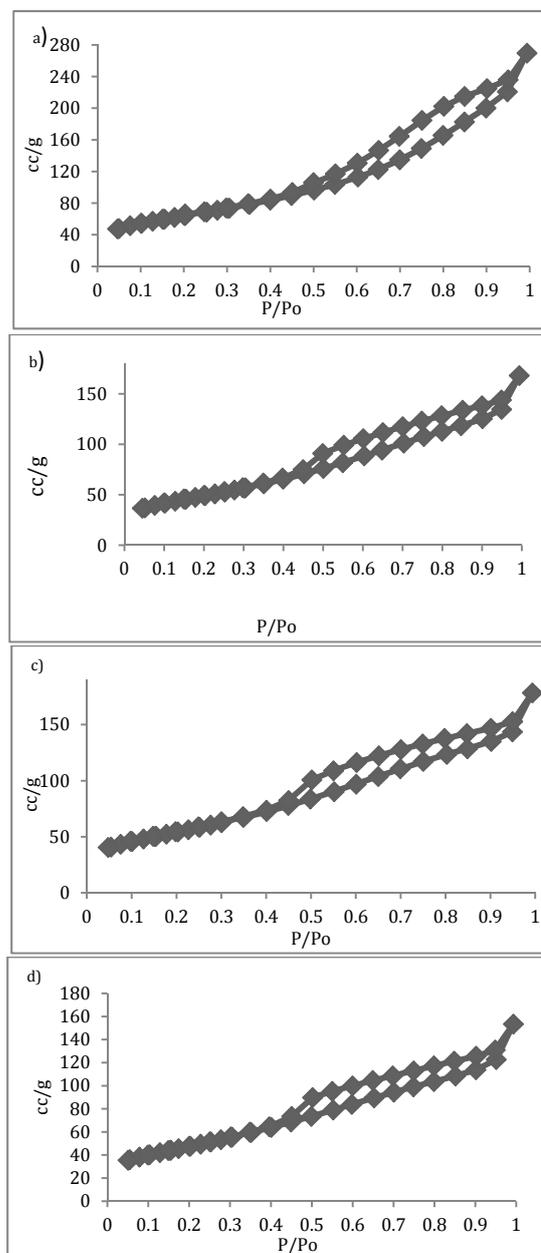
**Fig. 2:** SEM images of a) MMT K10, b) Cu-MMT K10, c) Al-MMT K10, d) Fe-MMT K10

### 3.3. Nitrogen sorption isotherms

Fig. 3 shows the nitrogen sorption isotherms of unmodified MMT K10 and modified samples. The isotherm of unmodified MMT K10 belongs to Type IV with type H3 hysteresis loop according to BET classification. The modified samples show a similar type of isotherm and hysteresis loop to that of unmodified MMT K10. This indicates that the porous structure of clay is still maintained even after the exchanged reaction (Borah et al., 2014), as already been revealed by XRD and SEM results. Type IV isotherm can be associated to with capillary condensation taking place in mesopores. The initial part of Type IV is attributed to monolayer-multilayer adsorption.

BET surface area and pore volume, obtained from the conventional analysis of nitrogen isotherms are collected in Table 2. Exchanged reaction resulted in decrease in the surface area and pore volume of the modified samples. It was suggested that the larger cation can eclipsed a certain surface of montmorillonite, which becomes unavailable for nitrogen molecules (Lee et al., 1999). Another possible reason for the decrease of the BET surface area is pore blocking effect; a larger exchange cation can clog some of the smaller pores. The decrease in the BET surface area of MMT K10 after cation exchanged is consistent with that of Joseph et al., 2005. Pore size distribution (PSD) curves from adsorption isotherm of unmodified MMT K10 and

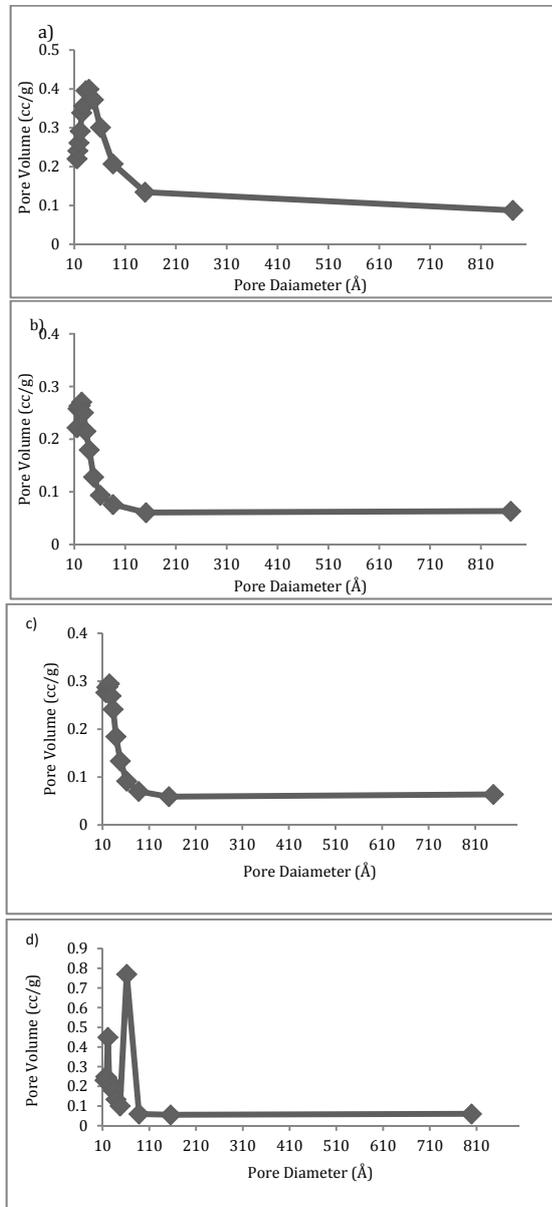
modified samples are illustrated in Fig. 4. The samples show the main peak at 15.55 Å to 21.27 Å, in addition, another one peak at 61.7 Å for Cu-MMT K10. According to IUPAC definition these pores are related to mesopores range (diameter of 20-500 Å) (Fatima et al., 2011; Dutta et al., 2011).



**Fig. 3:** nitrogen sorption isotherms of a) MMT K10, b) 0.75M Al-MMT K10, c) 0.75M Fe-MMT K10 and d) Cu-MMT K10

**Table 2:** Surface area, pore volume of MMT K10 and modified samples

Sample	Surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)
MMT K10	228.294	0.374
Fe-MMT K10	195.538	0.216
Al-MMT K10	175.770	0.218
Cu-MMT K10	172.013	0.192

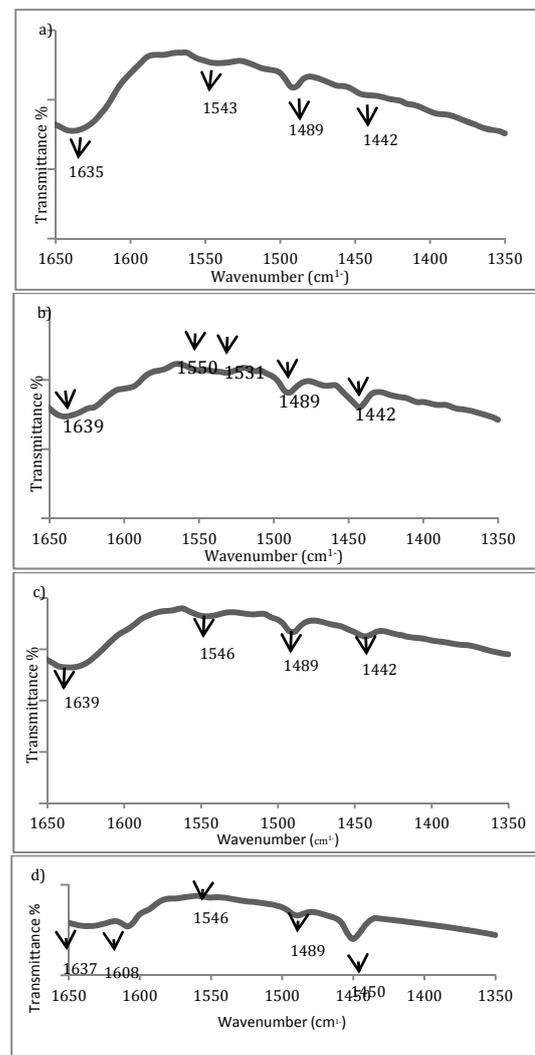
**Fig. 4:** Pore size distribution of a) unmodified MMT K10, b) Al-MMT K10, Fe-MMT K10 and Cu-MMT K10

### 3.5. Acidity of catalysts

Figure 6 shows the FTIR spectra of pyridine adsorption for unmodified and modified MMT K10 samples in the region from 1350 to 1650 cm<sup>-1</sup>. FTIR spectra show the vibration band at 1442, 1450 and 1489 cm<sup>-1</sup> is related to Lewis acid site. While the bands at 1546 and 1639 cm<sup>-1</sup> is related to Brønsted acid sites. The peaks assignments were done based on previous work (Fatimah et al., 2011; Reddy et al., 2007; Reddy et al., 2009). Al-MMT K10 and Fe-MMT K10 showed bands at ~1546 and 1639 cm<sup>-1</sup> due to

Brønsted acid sites. The Lewis acid sites which at ~1442 cm<sup>-1</sup> was almost as intense as that for Brønsted acid site. However the band at 1489 cm<sup>-1</sup> due to both the Brønsted and Lewis acid sites, the intensity of this band is slightly more than the other two bands of Lewis and Brønsted acid. Cu-MMT K10 showed increasing in Lewis acid band with appearance of peak centered at 1450 cm<sup>-1</sup>.

A new band around 1608 cm<sup>-1</sup> was also observed for Cu-MMT K10 sample which due to coordinated pyridine to the metal ions through aromatic  $\pi$ -electrons (Shimizu et al., 2008; Reddy et al., 2009). This extra band was not observed in the other exchanged samples. The Lewis acid sites in all modified samples were increased as compared to unmodified MMT K10, this due to the ability of these guest cations 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. Study conducted by Shimizu et al. (2008) has reported that the Lewis acid sites can be increased by changing the exchangeable cation by high hydration cations.

**Fig. 5:** FTIR pyridine spectra of MMT K10 and modified samples where a) MMT K10, b) Al-MMT K10, c) Fe-MMT K10, and d) Cu-MMT K10

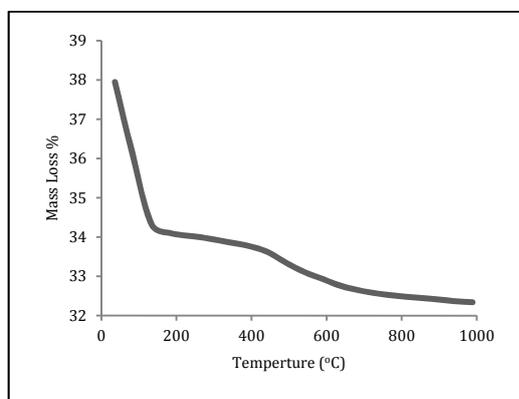
### 3.6. Thermal analysis

TGA was conducted to determine the effect of the  $M^{n+}$  modification on the thermal stability of the MMT K10 clay. Fig. 6 shows TGA curve of unmodified MMT K10 and as there is no significant difference in the weight loss trend between unmodified and modified MMT K10, the other samples are not shown here. All samples have two mass loss steps, in the range from 20-1000 °C; the thermal transition steps of the examined samples are demonstrated in Table 3. The first step in the range from 40-290 °C is related to the desorption of water molecules bounded to the exchangeable cations in interlayer space (Kuzminska

et al., 2014; Molu et al., 2010; Eng et al., 2013). While the second step ca. between 280 °C and 1000 °C can be assigned to the dehydroxylation of -OH groups of MMT K10 clay (Zatta et al., 2013; Virkutyte and Varma 2012). After that the weight of the samples remained almost constant in further undergone to thermal treatment. From table 3, 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  $M^{n+}$  [21]. 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 3:** TGA results of MMT K10 and modified samples

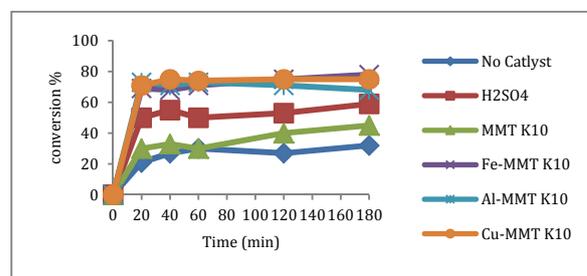
MMT K10	Step 1		Step 2	
	Mass loss %	Temp °C	Mass loss %	Temp °C
Unmodified	14.09	39-284	4.29	285-987
0.75 M Fe	8.20	37-299	3.85	299-982
0.75 M Al	10.34	37-299	4.35	298-973
0.75 M Cu	5.33	37-299	3.34	299-982



**Fig. 6:** TGA curve of unmodified MMT K10

### 3.7. Catalytic activity

Esterification of stearic acid with methanol using unmodified MMT K-10, M-MMT K-10 samples and homogenous catalyst i.e.  $H_2SO_4$  were conducted. It can be seen that M-MMT K-10 samples were able to give the highest stearic acid conversion up to 70% compared to the esterification without catalyst (blank reaction), unmodified MMT K-10, and  $H_2SO_4$  (Fig. 7). As can be seen, all the modified samples gave higher acid conversion from the first of 40 minutes of the reaction time compared to the other tested catalysts. Refer to the pyridine adsorption results which all the modified samples showed increased in the Lewis acid sites compared to unmodified MMT K10. Significant drop in surface area and pore size of the modified MMT K10 have no effect to the activity of the catalysts. Furthermore, it requires relatively low temperature i.e. 80 °C 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 is much more favorable compared to corrosive  $H_2SO_4$ .



**Fig. 7:** Conversion profiles of esterification of stearic acid with methanol

### 4. Conclusion

The  $M^{n+}$ -MMT K-10 samples were successfully synthesized by exchanged process and characterized using XRD, SEM/EDX,  $N_2$  sorption isotherm and surface acidity. The obtained results show that the structure of MMT K10 was not affected during cation exchanged reaction. It has been seen that the modified MMT K10 showed an outstanding result in esterification reaction compared to unmodified MMT K10 and homogeneous catalyst  $H_2SO_4$ . It can be concluded that cation exchanged MMT K-10 proved to be inexpensive, efficient and potential heterogeneous catalyst for esterification reaction to replace the usage of potentially hazardous homogeneous catalyst.

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