

# Using of Clay as Heterogeneous Catalysts for Organic Syntheses; A Review

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## Article History

Received: February 19, 2021

Revised: April 14, 2021

Accepted: April 17, 2021

Published: April 19, 2021

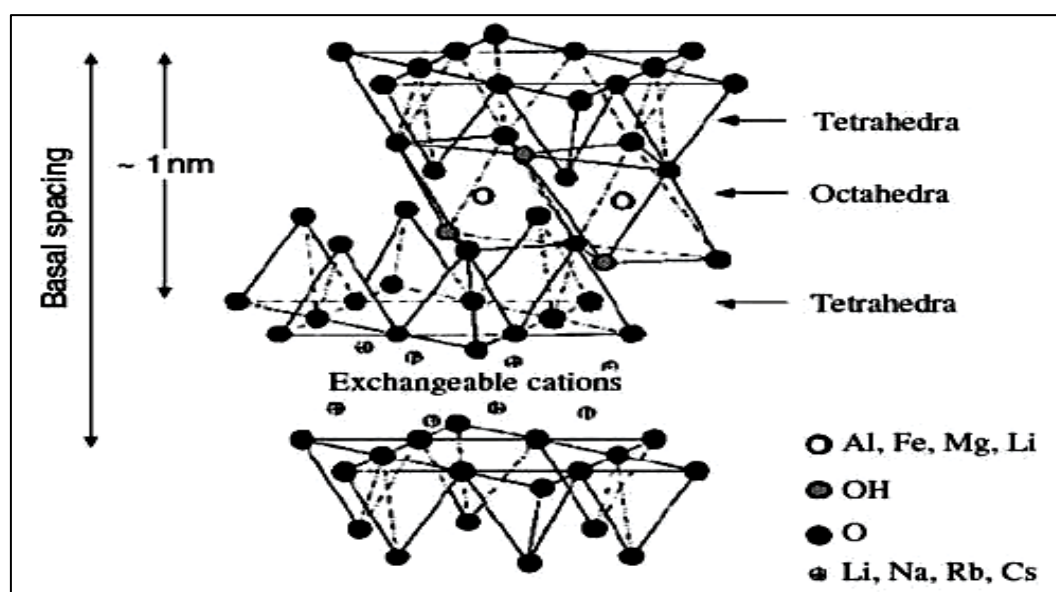
## Abstract

Clay and clay modified catalysts have been widely used to catalyze various types of organic reactions such as esterification reactions, isomerization reactions, cyclization reactions, oxidation of alcohols, dehydrogenation, epoxidation and several more. Due to its favorable properties such as low cost, thermal stability, selectivity, large surface area, ion exchange capacity, easily separated, as well as environmental friendly. This paper reviewed some recent studies on the using of clay and modified clay as catalyst for the production of esters.

**Keywords:** Clay; Modified clay; Heterogeneous catalyst; Organic syntheses; Ester production.

## 1. Introduction

Montmorillonite (MMT), the major clay mineral commercially available has been used as an effective heterogeneous catalyst for many chemical reactions in organic synthesis due to its physicochemical properties. It is a layered aluminosilicates that can be classified as 2:1 type dioctahedral smectites group (Figure 1). The MMT K10 crystalline structure consists of two silica tetrahedral sheets sandwiching an octahedral sheet of aluminium. It is known as the T-O-T sheets that can be classified as 2:1 type dioctahedral smectites [1]. Cations  $\text{Si}^{4+}$  and  $\text{Al}^{3+}$  fill tetrahedral sheet, while two-thirds of the octahedral sheet filled with  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$  or occasionally other elements in octahedral coordination. The exchangeable cations and water molecules filled the space between the two sheets. 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  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{3+}$  [2-6]. This property makes the MMT as a suitable heterogeneous catalyst for many chemical reactions such as the rearrangement or isomerization reaction, synthesis of the heterocyclic compound, ether formation, acetalization and esterification reaction [7].



Source: Singla, et al. [8]

Montmorillonite K10 is an acid treated montmorillonite refluxed in an acidic solution; the acids that can be used include hydrochloride acid, sulphuric acid, and nitric acid [9]. There are considerable methods which can be used to modify MMT to improve its catalytic properties. The surface modifications of MMT have received great attention because these allow the production of new materials which can be used for many applications. Such of these methods include cation exchange, pillaring, and acid activation. The cation exchanged MMT K10 is considered as efficient catalysts due to its reusability without losing its activity, also increasing the strength of Lewis acid site [10].

The esterification reaction normally carried out using homogeneous Brønsted acid catalysts such as sulfuric acid, but using such this catalyst has some difficulties such as the corrosion of equipment, waste generation and environmental problems [11]. 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 the esterification of long chain acid for example sulphated zirconia has been studied in the esterification of oleic acid with methanol [12], raw halloysite as a catalyst for esterification of lauric acid [13], and zirconia-modified silica in esterification of oleic acid with trimethylolpropane [14]. This present paper aims to review and summarize effects of MMT K10 and modified MMT K10 clay catalysts in esterification reaction and the reports that have been published on them.

## 2. Heterogeneous Catalysts

There are two main categories of catalysis; homogeneous catalysis which the catalyst is in the same phase with the reactants, and heterogeneous catalysis which the catalyst is present in a different phase from the reactants in the reaction. Heterogeneous catalysts are widely used in promoting various chemical reactions. It has received an intense attention by researchers in studying its catalytic activity and to improve its performance. This is due to numerous advantages that can be seen upon the usage of a homogeneous catalyst. According to Bahramian, *et al.* [15], there are many benefits of heterogeneous catalysts such as high selectivity, easy catalyst separation, long catalytic life, thermal stability and the heterogeneous process which is more environmentally friendly. Despite many remarkable findings of work that researchers and chemists poured upon their studies in developing a complex and newly synthesized heterogeneous catalyst, a naturally occurred catalyst gained its own place. One of the most widely used and highly recognized heterogeneous catalysts in the chemical reaction comes from soil, the clay catalyst. Clay is a preferable heterogeneous catalyst to replace the homogenous catalyst due to their properties such as easily available, inexpensive and easy modification [4].

## 3. Clay Catalysts

The extensive demand for a cleaner environment is forcing the chemical industry to use less hazardous, low cost and environmentally friendly materials. Clay mineral constitutes one of these materials. Clay mineral is a group of aluminosilicates that have been widely used as heterogeneous catalysts for many types of organic synthesis, due to their favourable properties such as low cost, thermal stability, selectivity, large surface area, easily separated as well as environmentally friendly [16].

Clay catalyst was proven to have both the Lewis and Brønsted acid sites. The Lewis acidity is due to the cations at the crystal edges and this acid site can be enhanced by the exchange of the interlayer cations i.e.  $\text{Na}^+$  and  $\text{Ca}^{2+}$  with  $\text{Al}^{3+}$  ion by the reaction of clay with  $\text{AlCl}_3$  solution. While the Brønsted acid character of clays arises mainly due to the dissociation of the intercalated water molecules coordinated to cations [17]. The presence of hydroxyl group (-OH) on the surface of clay minerals make it as a hydrophilic material, which can link very easily to the water molecules. The chemical properties of clay minerals such as the acidity which is due to the presence of Lewis and Brønsted acidity, hydroxyl groups, and the type of exchangeable cations, make the clay catalysts as suitable heterogeneous catalysts for many chemicals and industry applications [18]. There are many types of clay minerals; and they can be divided into various groups depending on the layer type. The important groups of clay minerals are listed in Table 1 [19].

Table-1. Classification of clay minerals

Group name	Structure	Composition
Kaolinite	1:1	$\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_8$
Smectite (MMT)	2:1	$\text{M}_x(\text{Al}_{2-x}\text{Mg}_x)(\text{Si}_4)\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$
Pyrophyllitic	2:1	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$
Talc	2:1	$\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$
Mica	2:1	$\text{X}_2\text{Y}_4\text{Si}_6\text{Al}_2\text{O}_{20}(\text{OH})_4$ (X= K and/or Na, Y=Al and /or Fe and /or Mg)
Chlorite	2:2	$(\text{Mg}_{6-y-x}\text{Fe}_y\text{Al}_x\text{Si}_{4-x})\text{O}_{10}(\text{OH})_8$
Serpentine	1:1	$\text{Mg}_6\text{Si}_4\text{O}_{10}(\text{OH})_8$

## 4. MMT K10 and Modified MMT K10 Catalysts

MMT K10 is an acid- treated montmorillonite refluxed in one of these acids solutions; sulphuric acid, hydrochloric acid and nitric acid [9]. MMT K10 is one of the important catalytic materials in the heterogeneous catalysis due to its low cost and environmental conservation. It has some unique properties such as cation exchange capacity and swelling ability, therefore accommodating various guest species in its interlayers [20]. MMT K10 can be further modified to improve its properties. The surface modifications of MMT K10 have received attention

because this allows the production of new materials which can be used for many applications [21]. There are considerable methods which can be used to modify MMT K10 such as pillaring, acid activation and cation exchange. Modified MMT K10 has been widely used as a heterogeneous catalyst for numerous organic syntheses. The acid activated MMT K10 has been used as a heterogeneous catalyst on the esterification of 4-hydroxy benzoic acid (HBA) with three different type of alcohols i.e. methanol, ethanol and propanol to the synthesis of parabens [22]. The MMT K10 was activated using 25 ml of HCl at 60 °C for 5 hours. The catalyst was able to give high yields of parabens up to 80%. Aher, *et al.* [10], piloted a study on the copper exchanged MMT K10 as a catalyst for the direct carboxylation of terminal alkynes with carbon dioxide. The carboxylation reaction in this study was carried out using phenyl acetylene treated with (10 wt %) Cu-MMT K10, CO<sub>2</sub> (1 atm) and Cs<sub>2</sub>CO<sub>3</sub> in *N,N*-dimethylformamide (DMF; 3 ml) at 60 °C. The yield of acetylenic carboxylic acid was 30% and with the increasing of catalyst amount to 20 wt % the yield was increased to 74%. Further increase in the amount of catalysts to 30 wt % resulted in increasing the yield to 94%. Shimizu, *et al.* [6] conducted a study on using the cation exchanged MMT K10 as a heterogeneous catalyst for the acetylation of alcohol. The cations used were H<sup>+</sup>, Al<sup>3+</sup>, Fe<sup>3+</sup>, Ce<sup>4+</sup>, Yb<sup>3+</sup>, Sc<sup>3+</sup>, Y<sup>3+</sup>, Mn<sup>2+</sup>, La<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup> and Na<sup>+</sup>. The catalyst showed an increase in the Lewis acid sites; the acidity was monitored by IR using pyridine, acetonitrile and acetone. Among the modified catalysts, Fe<sup>3+</sup>-MMT K10 was the most effective towards the acetylation of cyclohexanol with acetic anhydride at room temperature. The catalyst showed a high acetylation yield above 92% after 24 hours.

## 5. Esterification Reaction Using MMT Catalyst

The study of the esterification of acetic acid with ethanol was conducted by Gurav and Bokade [23] using heteropolyacid i.e. dodecatungstophosphoric acid (DTPA) supported on MMT K10. The modified samples prepared were varied in terms of the composition of the heteropolyacid, which was 10%–30% w/w DTPA/MMT K-10. The study found that 20% w/w DTPA/MMT K-10 was the efficient catalyst with 90% acetic acid conversion and 100% ethyl acetate selectivity.

Acid activated MMT clay has been used for the esterification of acetic acid with ethanol [24]. In this study MMT clay was activated by treating with 1 M H<sub>2</sub>SO<sub>4</sub> and heated in an oven at 373 K for 4 hours. The reactions were carried out in a water bath for 6 hours at 80 °C and 90 °C with catalyst masses of 0.15 g and 0.3 g and the mole ratios of acid to alcohol were 1:1 and 1:4. The result showed that the increase in the temperature and mole ratio of acid to alcohol showed an increase in the acid conversion. Fatimah and Wijaya [25] conducted a study on alumina pillared MMT by varying the Al<sup>3+</sup> contents in the samples. They concluded that the pillarization process showed significant improvement on the physicochemical character of MMT. The pillared MMT gave high activity in the esterification reaction of acetic acid and ethanol relative to unmodified MMT. Titanium pillared bentonite was used as a catalyst for the esterification of acetic acid with ethanol [26]. The titanium pillared bentonite was prepared by modification of bentonite by titanium pillaring solution at 500 °C. The results revealed significant improvement in the physicochemical characteristics of the bentonite on pillared catalyst compared to the unmodified. The pillared sample showed an increased in d-spacing, surface area, pore volume and the catalytic activity. The Ti-pillared catalyst showed a high acid conversion about 45% than that observed for the unmodified catalyst 15%. The esterification of phenylacetic acid with phenol, cresols, nitrophenols and resorcinol have been studied by Reddy, *et al.* [27] using the MMT exchanged with H<sup>+</sup>, Al<sup>3+</sup> ions and polyhydroxy oligomer cations of Al<sup>3+</sup> to get pillared MMT. The Al<sup>3+</sup>-MMT compared with the unmodified MMT showed a high ester yield 67% at 6 hours of reaction time using *p*-cresol while the unmodified and pillared sample did not show any activity even 16 and 12 hours of reaction time respectively. The high activity of Al<sup>3+</sup>-MMT is due to the presence of high electronegative and polar Al<sup>3+</sup> ion which produces Brønsted acidity. This study also evaluated the effect of molar ratio of phenylacetic acid to *p*-cresol; 1:1, 1:2, 1:3, 1:4, 4:1, 3:1 and 2:1. Also was evaluated the effect of reaction time from 2 to 18 hours and different substituted phenols used. Among the cresols, *p*-cresol gave the highest yield of 77%. Reddy, *et al.* [5] continued their work on the esterification of succinic anhydride to di-(*p*-cresyl) succinate over M<sup>n+</sup>-MMT clay catalysts (M<sup>n+</sup>= Al<sup>3+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup>, Mn<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup> and H<sup>+</sup>). Among the M<sup>n+</sup>-MMT catalysts the Al<sup>3+</sup>-MMT and H<sup>+</sup>-MMT were found to be the most active for the esterification of succinic anhydride with *p*-cresyl with 75% yield of esters, 3:1 mole ratio of *p*-cresyl to succinic anhydride, catalyst amount 0.5 g and reaction time 8 hours. While in 2007, Reddy *et al.* conducted another study on the surface acidity of M<sup>n+</sup>-MMT (M<sup>n+</sup>= Al<sup>3+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup> and H<sup>+</sup>) and their catalytic activity towards the esterification of succinic acid with *iso*-butanol. The conclusion drawn from this study was that trivalent cation exchanged has strong Brønsted acidity and thus gave the highest ester yield 96%, whereas the divalent cation exchanged showed a strong Lewis acidity and the lowest esters yield 27%. Modified MMT K10 was used as a catalyst in the esterification of stearic acid with methanol. The same catalysts were used to reduce the acidity of enhanced free fatty acid FFA sunflower oil (28). MMT K10 was acid activated using H<sub>2</sub>SO<sub>4</sub>, the acid activated catalysts prepared by two processes. The first process MMT K10 was refluxed with 200 ml of 0.25 M H<sub>2</sub>SO<sub>4</sub> for 3 hours, then dried at 373 K in the air oven and calcined at 773 K for 10 hours MMT K10 (I). The second process MMT K10 was activated in an oven overnight at 373 K then 0.1 ml of concentrated H<sub>2</sub>SO<sub>4</sub> was added with stirring after that the sample (MMT K10 (II)) was kept protected from the moisture until use. The study concluded that the catalyst was able to be an effective catalyst with 95% of methyl stearate obtained using MMT K10 (II). This catalyst also showed the ability for the reduction of FFA from 11 to 4% due to 94% FFA conversion to fatty acid methyl esters. Using modified MMT K10 catalyst with the two waste oils showed the ability of these catalysts to reduce the acidity of these oils. Enas *et al.*, [28, 29] 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, Al and Cu. Furthermore, it requires relatively low temperature i.e. 80 °C and only a short time to achieve maximum conversion.

## 6. Conclusion

It can be concluded that MMT K-10 and modified MMT K-10 clay proved to be inexpensive, efficient and potential heterogeneous catalyst for esterification reaction to replace the usage of potentially hazardous homogeneous catalyst. So using the catalysts prepared from simple and natural clay modified with the earth mineral i.e. Fe<sup>3+</sup>, Cu<sup>2+</sup>, Al<sup>3+</sup>, Zn<sup>2+</sup> and Ni<sup>2+</sup>. 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 for many of organic synthesis.

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