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Effect of Calcination Temperature and Tmaoh on Catalytic Activity of Basic Clay

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Abstract: Montmorillonite K10 was intercalated with lithium hydroxide and used for the transesterification Methyl Laurate (ML) with glycerol. This modified clay was characterized to elucidate the influence of added Tetramethylammonium Hydroxide (TMAOH) on its catalytic activity. Effects of calcination temperature (350-650°C) on the catalytic properties of basic clay were investigated with the goal of determining the optimum pretreatment conditions. The basic clay calcined at 450°C exhibited the optimum activity when used together with TMAOH. The results showed that TMAOH played an important role in improving the efficiency of the basic clay. By using a glycerol/methyl laurate ratio of 8:1 without any addition of TMAOH at a temperature reaction of 130°C, 60.1% methyl laurate conversion and 56.5% selectivity to monolaurate were achieved over the LiK10 calcined at 450°C for 5 h. Meanwhile, the addition of TMAOH increased the ML conversion and selectivity to monolaurate to 82.5 and 88.2%, respectively.

Key words: Clay, LiOH-montmorillonite, transesterification, glycerol monolaurate, selective synthesis

INTRODUCTION

Monoglycerides are non ionic surfactants which have important applications as emulsifier in food, pharmaceutical and cosmetics production due to their physicochemical properties, basically the hydrophilic/hydrophobic balance (Lauridsen, 1976; Ahmed *et al.*, 2000). These esters are generally manufactured on industrial scale by continuous glycerolysis of fats and oils at high temperatures (220-250°C) using alkaline catalysts under a nitrogen gas atmosphere (Sonntag, 1982). Since the required product is the highly pure monoglyceride, the mixture is molecular distilled to obtain higher monoglycerides purity (~80%) (Fregolente, 2007).

A number of solid bases have been used as catalysts for the transesterification of glycerol in order to avoid drawbacks associated with the use of homogeneous catalysts such as low yield, dark color and burnt taste. Abro *et al.* (1997) and Barrault *et al.* (2004) showed that basic solid catalysts such as MgO, CeO₂ and La₂O₃, as well as alkali-doped MgO (Li/MgO and Na/MgO) were active catalysts for the transesterification of methyl stearate with glycerol. The authors also noted that the

nature of the oxide had a small effect on monoester selectivity, and that the distribution of the esters obtained was similar to that obtained with homogeneous basic catalysts.

Corma *et al.* (2005) reported that the glycerolysis of triolein with glycerol could be carried out over solid basic catalyst such as hydrotalcites. Al-Li mixed oxide resulted in an active Lewis base catalyst with better performance than MgO and hydrotalcite. From these heterogeneous catalytic routes, glycerol esters were obtained at 90% yield with 75% selectivity to onoglycerides. However, high temperature and a glycerol/triolein molar ratio of 12 were necessary to reach such results.

In its origin or modified forms, montmorillonite K 10 is a type of acidic stratified silicate mineral with a three-layer structure with an ideal chemical formula of (Al₂₋₃Mg₇) Si₄O₁₀ (OH)₂•nH₂O which widely used as adsorbent (Fan *et al.*, 2006) as acid catalyst, or as catalyst support (Iqbal *et al.*, 1988; Choudhary *et al.*, 2004; Bahulayan *et al.*, 2003; Bokade and Yadav, 2009; Fatimah *et al.*, 2009). In its natural form, montmorillonite K 10 clay is Brønsted acidic but it can be easily made basic by treating them with a basic cation-containing solutions e.g., K₂CO₃ (Dintzner *et al.*, 2006), NaOH, KOH

and LiOH (Beavers and Culp, 2004). However, the use of a basic clay catalyst in the glycerolysis often results in the adsorption of glycerol which can reduce the activity of catalyst. Aserin *et al.* (1984) synthesized monoglyceride by using a Phase Transfer Catalyst (PTC) to overcome the drawback of low solubility of fatty acid salt in epichlorohydrin. Over 90% of pure non food monoglycerides had been obtained in quantitative yields after short reaction time at relatively low temperature. However, it should be noted that monoglycerides prepared by this method are not food grade. The use of aqueous alkali and PTC in organic reaction has been reported by some researchers. It was reported that the presence of PTC was of great importance in the saponification of vegetable oil using aqueous alkali catalyst (Bhatkhande and Samant, 1998) and hydrolysis of small amount of lipid using organic basic solution (Woo *et al.*, 2002). Lopez and Pleixats (1998) presented that treatment of sultam-derived N-(diphenyl-methylene) glycinate equivalent to 1 with activated organic bromides and with Michael acceptors under solid-liquid PTC conditions using potassium carbonate as base, produced monoalkylated compounds with high diastereo selectivity (>97%). Zhang *et al.* (2009) also demonstrated that base-catalyzed transesterification rate for biodiesel synthesis was enhanced with PTCs such as cetyltrimethylammonium bromide, tetrabutylammonium hydroxide and tetrabutylammonium acetate. The use of basic clay with PTC provides a potential enhancement of the clay mineral properties. The surfactant interacting with surface of the clay particles can influence the stability and the flow behavior of clay-water system (Alemdar *et al.*, 2000). Clay mineral presents a proton rich environment when mixed to organic molecules. On the other hand, the catalytic abilities can be improved by providing organic cations in the interlamellar space, which enable the access to/and interact effectively with organic molecules.

Herein, we elucidate the role of TMAOH on a base modified clay-catalyzed transesterification of methyl ester with glycerol. The effects of parameters such as type of calcinations temperature, amount of TMAOH and other variables are thoroughly discussed.

MATERIALS AND METHODS

Reagents and material: Glycerol (99%), Methyl Laurate (ML) (98%) and montmorillonite K 10 used in this study were purchased as commercial products of Fluka. Lithium Hydroxide (LiOH) and Tetramethylammonium Hydroxide (TMAOH) were purchased from Merck. All the above materials were used without further purification. Deionized water was used throughout this work.

Preparation base modified clay: A 250 mL round bottom flask equipped with a reflux condenser was charged with 10 g of Montmorillonite K10 clay, 100 mL deionized water and an amount of LiOH solution. This mixture was stirred and heated at reflux for 6 h. The slurry was then allowed to cool to room temperature. Next, the solid were separated from liquid by centrifugation and the liquid portion was decanted and discarded. The solids were then washed by resuspending in 500 mL of deionized water followed by centrifugation. This sequence was repeated for two more times to ensure complete removal of all soluble species. The base modified clay (Li-K10) was calcined in an oven at 350, 450, 550, 650°C for 4 h to complete the work up.

Characterization of catalyst: Base strengths of the catalysts (H_-) were determined by using Hammett indicators. About 25 mg of the catalyst sample was shaken with 5.0 mL of a solution of Hammett indicators diluted with methanol, and left to equilibrate for 2 h. After the equilibration, the color on the catalyst was noted. The following Hammett indicators were used: neutral red ($H_- = 6.8$), bromthymol blue ($H_- = 7.2$), phenolphthalein ($H_- = 9.3$), 2,4-dinitroaniline ($H_- = 15.0$) and 4-nitroaniline ($H_- = 18.4$).

Thermal Gravimetric Analysis (TGA) data of K 10 and base modified clay samples were taken using a thermal analyzer (TGA7 Perkin Elmer) instrument by heating the samples at 20°C min⁻¹ heating rate from ambient temperature to 850°C under a high-purity nitrogen flow at 20 mL min⁻¹.

Catalyst test: The transesterification reactions of glycerol with methyl laurate were accomplished in a glass jacketed reactor equipped with a condenser system. Glycerol, methyl laurate and catalyst (4% wt) were mixed under magnetic stirring and heated in a silicone bath to the required temperature in absence of any solvent. A Dean-Stark instrument was attached to the batch reactor to remove methanol that was formed during the reaction. After the 5 h reaction, samples of 100 µL were withdrawn from reaction vessels and transferred into a sample vial containing 100 µL of water and 100 µL of methyl acetate using a method adopted from Yang *et al.* (2003). The samples were then vortexed, and the organic phase containing acylglycerols and FA was separated by means centrifugation. To this, 0.1 mL of 0.2 M internal standard and 0.5 mL acetone were added and then, a 1 µL sample was injected into a gas chromatograph.

The product composition was analyzed using a Hewlett Packard instruments HP 5800 gas chromatograph equipped with an FID. The column used was Zebron ZB-5HT Inferno (5%-Phenyl- dimethylpolysiloxane

nonpolar, 15 m×0.32 mm i.d.×0, 1 μm df). The temperatures of the injector and detector were set at 250 and 280°C, respectively. The temperature of the column was held at 100°C for 0.5 min, increased to 330°C at a rate of 10°C min⁻¹ and then maintained at 330°C for 3 min. The split ratio used was 1:5. The degree of transesterification was expressed as the ratio of the amount of ML consumed in the reaction to the initial amount of ML before the reaction. The MG and DG contents were expressed as the sum of the wt. % of their regioisomers. The authentic standards TG, DG, MG and FA were additionally used for identification.

RESULTS AND DISCUSSION

TGA result: One method for the characterization of basic clay is by the use of thermal analysis technique. Such technique can be used to evaluate the thermal stability of the basic clay and the characteristics of the thermal decomposition process. Changes in the basic clay structure and thermal character are related to three respective factors i.e., type of interlayer cation, interlayer cation radius, and the movement of the interlayer cation (Emmerich *et al.*, 1999). TGA/DTG results of the five clays catalyst are shown in Fig. 1 and 2. All the clay catalysts showed an initial weight loss in the temperature range of 30-120°C with K 10 exhibited a highest weight loss (ca. 11%). The initial weight loss was first attributed to the volatilization of both adsorbed water from the external surface and the water residing inside the interlayer space coordinated to the exchangeable cations such as Na⁺, Ca²⁺ and Li⁺. Sharp weight drop at lower temperature for K 10 suggested that more water being physically adsorbed on the surface than that occurring in interlayer while Li K 10 calcined at 650°C showed least water adsorbed on the surface. This was due to heating of lithium saturated montmorillonite at a temperature higher than 500°C that caused the collapse of the interlayers and decreased the amount of water sorbed (Bujdak and Slosiarikova, 1994).

Furthermore, the acidic or basic character of montmorillonite depends largely on the nature of both the water of hydration and the exchangeable cation (Azzouz *et al.*, 2006). The lithium exchanges have neutralized substantially all of the acid sites (OH sites) within the clay and replaced them with their conjugate basic sites (O⁻) and impregnated the clay with cations from the base so that basicity of montmorillonite increased (Beavers and Culp, 2004). Calcination of lithium saturated montmorillonite released small and neutral molecules which are often anhydrides of inorganic acids. The acid anhydrides then reacted with the hydroxyl groups in the

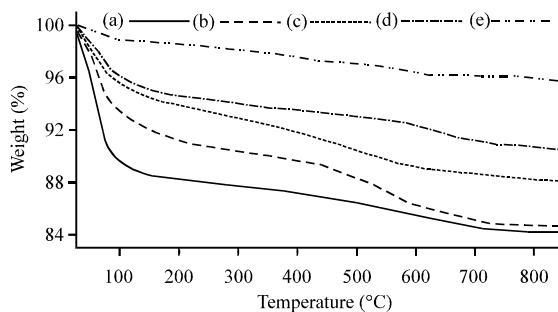


Fig. 1: TGA thermogram of (a) K10, (b) LiK10-350, (c) LiK10-450, (d) LiK10-550 and (e) LiK10-650

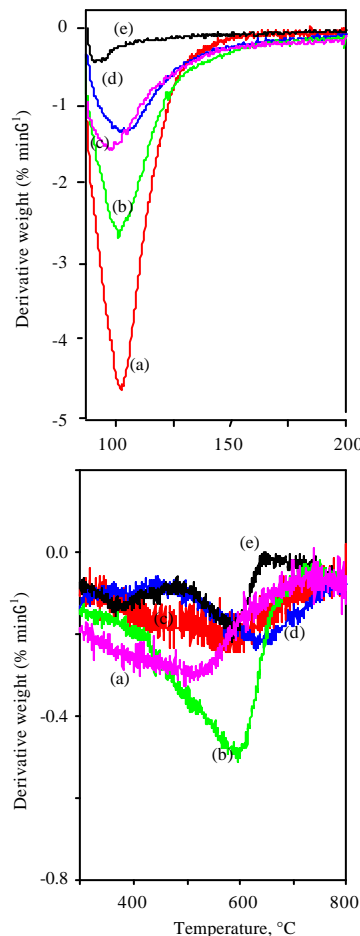


Fig. 2: DTG curve of (a) K10, (b) LiK10-350, (c) LiK10-450, (d) LiK10-550 and (e) LiK10-650

clay affecting the desired base-modification. Furthermore, the calcination of lithium saturated montmorillonite caused the migration of the Li⁺ cations from the interlayer

space to vacant lattice octahedral sites and reduced the net negative layer charge due to fixation of Li within the layers (Hrobarikova *et al.*, 2001). So the calcination of Li saturated montmorillonite affected water coordinated to Li⁺ ions in the interlayer is bonded more strongly and that water was liberated at higher temperature (>400°C) (Bujdak and Slosiarikova, 1994). Calcination at higher than 400°C also caused the removal of organic materials (Ahmed and Ramli, 2011). As demonstrated by DTG curves in Fig. 2 that the Li K 10 calcined at 350°C had higher peak for dehydroxylation of the silicate lattice at about 600°C.

The base strength and the activity of catalyst: Table 1 summarizes the basic strengths of a series of Li-K 10 catalysts calcined at different temperatures. The parent K 10 MMT was an acidic clay as it could not change the colour of bromthymol blue ($H_{-} = 7.2$). After the intercalation with LiOH followed by calcination at elevated temperature from 350 to 650°C, the intercalated clay samples exhibited significantly higher base strengths. The base strength of catalyst increased as the calcination temperature was increased, except for the Li-K10 calcined at 650°C (LiK10-650) that showed the weakest base strength (H_{-}) in the range of 7.2-9.3. It demonstrated that the Li-K 10 calcined at 450°C (LiK10-450) had the highest base strength. When the calcination temperature was higher than 550°C, the base strength decreased.

Subsequently, we conducted the catalytic activity tests for the monoglyceride synthesis at 130°C with an 8:1 molar ratio of the glycerol to methyl laurate. The catalytic activities data in Table 1 indicate the conversion of methyl laurate and the selectivity of monoglyceride after transesterification for 5 h. The experimental result indicated that calcination at 450°C for 4 h was the optimal condition for pre-treatment, in which the highest conversion of methyl laurate can be achieved. From this table, it can be observed that the maximum conversion of methyl laurate of 60.1%, was obtained at a calcination temperature of 450°C. Meanwhile, low level of conversion was observed at a calcination temperature below 350°C and above 650°C. Obviously, the basicity changes with calcination temperatures paralleled the change in the catalytic activity for the glycerolysis of methyl laurate. The data obtained by using Hammett indicator titration are in good agreement with the catalytic finding. Thus, the Hammett titration method could give qualitative information of the basic property of the solid catalysts.

Effect of the amount of TMAOH: The aforementioned results confirmed that an increase in basicity of the clay

Table 1: Catalytic activities and base strength of LiOH intercalated clay at different calcination temperatures

Catalysts	Basic strength (H_{-})	Yield (%)
LiK10-350	7.2 < H_{-} < 9.3	31.20
LiK10-450	9.3 < H_{-} < 15.0	40.00
LiK10-550	9.3 < H_{-} < 15.0	36.62
LiK10-650	7.2 < H_{-} < 9.3	21.03

Reaction conditions: glycerol/methyl laurate molar ratio, 8:1; catalyst amount, 3%; reaction temperature 130°C; reaction time, 5 h

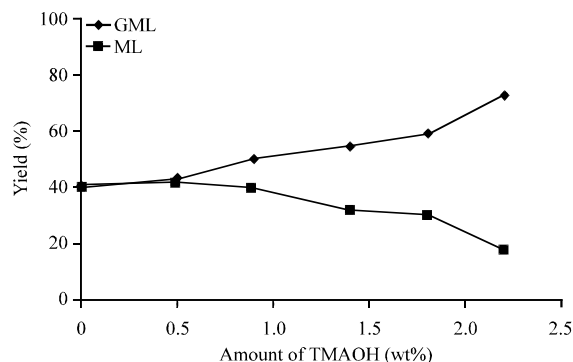


Fig. 3: Effect of the amount of added TMAOH on the yield of GML and ML respectively (Reaction condition: glycerol/methyl laurate molar ratio, 8:1; catalyst amount, 3 wt. %; reaction time 5 h; reaction temperature 130°C)

catalyst could only promote faster reaction rate while it did not favour the formation of monoglyceride. Thus, several experiments were performed in order to observing the influence of the tetramethylammonium hydroxide ($(CH_3)_4 N^+OH^-$) on the activity of the catalysts. For the monoglyceride synthesis using heterogeneous catalyst, the reaction mixture was a three-phase system: methyl laurate/glycerol/clay catalyst.

The presence of TMAOH and the clay catalyst resulted in a synergistic effect in catalyzing the reaction of the methyl laurate with glycerol. The effect of the addition of TMAOH could enhance the effectiveness of LiK10 catalyst on the conversion of methyl laurate and the selectivity of monolaurate. As shown in Fig. 3, the yield of GML increased with an increase in the TMAOH amount from 0.5 to 2.2%.

The enhanced activity observed was attributed to a simple addition of TMAOH and clay activities. It is postulated that TMAOH functions both as a co-catalyst, maintaining the basic environment needed to enhance the activity of the heterogeneous catalyst and as a co-solvent, minimize the mass transfer problem normally encountered in the heterogeneous system.

TMAOH is a strong base solution which has a high activity in transesterification reaction (Yang *et al.*, 2003). However, in the monoglyceride production which is a

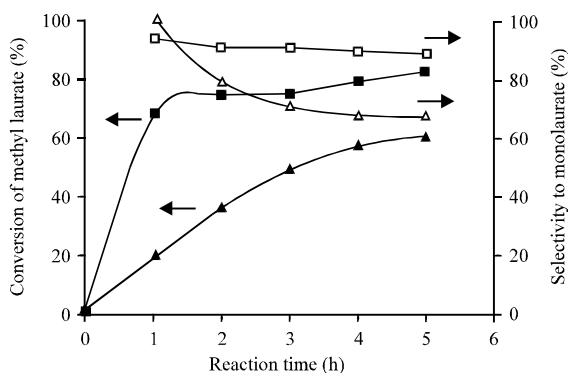


Fig. 4: Conversion and selectivity as a function of reaction time. (Reaction conditions: glycerol/methyl laurate ratio, 8:1; LiK10 450 amount 3% (■) with and (▲) without TMAOH 2.2%; reaction temperature 130°C)

reverse reaction of the biodiesel synthesis, the role of TMAOH appeared to suppress the di and triglyceride formations so that high selectivity of monoglyceride can result. Moreover, the different criteria such as the chain length, symmetry and lipophilicity could also determine the activity of PTC. The increased of lipophilicity was due to the presence of longer chain (Jayasree *et al.*, 1998). The lower lipophilicity of TMAOH was expected to result in high selectivity to monolaurate which have a high hydrophobicity than the reactants. Thus, the reaction and the selectivity of product were greatly enhanced by the addition of TMAOH.

We have shown that the presence of TMAOH enhanced the catalytic activity of LiK10-450. The swelling of montmorillonite immersed in glycerol suggested that the material had an affinity for this compound so that it was absorbed from the aqueous solution (Alemdar *et al.*, 2000). Even though the LiK10-450 was a hydrophobic clay, TMAOH was expected to reverse the adsorption of glycerol on clay. To check this, we added the TMAOH in the reaction and compared its activity for the glycerolysis of methyl laurate without that of LiK 10-450 catalyst (Fig. 4).

In Figure 4, the conversion versus reaction time is presented. It can be seen that the activity catalyst of LiK10-450 with added TMAOH was higher than that of experimental run without TMAOH. For the reaction system with TMAOH, the conversion increased steadily with reaction time ranging between 0 and 1 h and thereafter remained nearly constant as a result of nearly equilibrium conversion. The maximum conversion of methyl laurate was achieved after 5 h. The highest conversion was found to be about 82.5% and the selectivity to monolaurate was about 88.2%.

Based on the modern theories of phase transfer catalysis, the presence of TMAOH could assist in extracting the laurate anion in the organic phase via liquid anion exchange mechanism similar with as reported by Aserin *et al.* (1984). The initial rapid reaction was due to the initial presence of tetramethylammonium cation (Me_4N^+) that would ion pair in reaction involving hydroxide ion. TMAOH has two important roles in this kind of reaction (Jwo, 2003). Firstly, it provides a mechanism for transferring an anion into the organic phase that contains the reactive substrate. Secondly, and more importantly, the anion is introduced in a weak solvated resulting in highly reactive state of the reactants to promote faster reaction.

CONCLUSIONS

K10 intercalated with lithium hydroxide (LiK10) which was prepared by treating with a saturated aqueous basic solution of LiOH followed by calcination at high temperature in air showed high catalytic activities for the transesterification reaction. Based on the results of this work, the temperature of calcination could significantly affect the base strength and the catalytic activity of LiK10 catalyst. Higher calcination temperature of LiK10 could reduce the base strength and the activity of catalyst. The highest catalytic activity of LiK10 was obtained by calcining the catalyst at 450°C. The presence of TMAOH in the reaction could improve the activity of catalyst. The reaction rate and monoglyceride selectivity were significantly enhanced by the addition of a small amount of TMAOH. In the absence of a TMAOH, the conversion was low as a result of the limited contact of glycerol and methyl laurate.

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