



Effect of tetramethyl ammonium hydroxide on the activity of LiOH-intercalated montmorillonite catalyst in the transesterification of methyl laurate with glycerol

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ABSTRACT

Montmorillonite K10 was intercalated with lithium hydroxide (LiK10) and used as catalyst for transesterification of methyl laurate with glycerol. Effects of calcination temperature (250–650 °C) and tetramethyl ammonium hydroxide (TMAOH) addition (0.5–2.2 wt.%) on catalytic activity were particularly elucidated. Successful intercalation of Li leading to improved water hydration was demonstrated. Calcination temperatures above 450 °C could reduce the basic strength and activity of LiK10 catalyst. Significant losses of porosity and basicity were attributed to excessive loss of hydrated water. Higher basicity of the catalyst led to better reactant's conversion but poorer selectivity to glycerol monolaurate (GML). TMAOH addition improved the activity of the catalyst and selectivity to GML. At a glycerol/methyl laurate ratio of 6.5:1 and 130 °C, 40% GML yield was achieved in 5 h. The addition of 2% TMAOH increased the yield to 89.9%. An increase in reaction temperature beyond 130 °C would reduce the catalytic activity due to a decrease in the surface tension of surfactant and its partial degradation. Thus, TMAOH could significantly improve activity of LiOH–MMT catalyst with corresponding improvement in selectivity to GML.

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1. Introduction

Glycerol esters of fatty acid have important applications in food, cosmetics, pharmaceutical and textile and fiber industries due to their polyfunctional nature and emulsifying, complexing, and lubricants properties [1]. These esters are generally prepared either through hydrolysis of triglyceride, esterification of glycerol with fatty acids or by glycerolysis of triglycerides i.e. transesterification of glycerol with fatty methyl esters. Transesterification process is a base catalyzed reaction. Industrial esterification and transesterification processes generally involve the use of homogeneous acid catalyst (e.g. sulfuric, phosphoric, or organic sulfonic acid) or homogeneous basic catalysts (e.g. KOH, NaCH₃O or Ca(OH)₂), which often leads to product mixtures containing 40–60% monoglycerides, 30–45% diglycerides, 5–15% triglycerides, 1–5%, 1–5% free fatty acids and/or their salts, and 2–10% glycerol [2]. Pure monoglycerides can generally be obtained by molecular distillation process which further raises the production cost [3]. The drawbacks associated with the use of homogeneous catalysts are the need for a neutralization step, the formation of soaps, high salt content in the product and the generation of wastewater that deserves further treatment [4,5].

Several attempts have been made to minimize problems associated with the use of homogeneous catalytic process by developing heterogeneous catalyst systems. The use of solid base catalysts is a promising approach to replace alkaline homogeneous catalysts. It helps in minimizing soap formation, difficulty in product separation, corrosion and environmental problems. At laboratory scale, some studies involving solid base catalysts have been reported including MgO, CeO₂, La₂O₃, as well as alkali-doped MgO (Li/MgO and Na/MgO). These catalysts are generally found to be active catalysts for the transesterification of methyl stearate with glycerol [6–8]. The authors also reported that the nature of these oxides had small effects on monoester selectivity. Usually, active catalysts could promote the formation of di- and triglycerides to result in poor selectivity to monoglyceride. The distribution of the esters obtained was also reported to be similar to that obtained with homogeneous basic catalysts.

Corma et al. [9] reported that the glycerolysis of methyl oleate with glycerol could be carried out over solid basic catalyst such as hydrotalcites. However, Al–Li mixed oxide catalyst resulted in an active Lewis base catalyst with better performance than MgO and hydrotalcite catalysts. From this heterogeneous catalytic route, glycerol esters were obtained at a yield of 80% with 80% selectivity to monoglycerides. The main weakness with respect to this process is high reaction temperature (around 200 °C) needed to obtain reasonable activity.

Recently, there has been considerable interest to use clays to catalyze organic reactions [10]. Clays, either natural or modified,

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are important and versatile low-cost materials with a wide variety of applications as catalyst or catalyst supports. Montmorillonite (MMT), a natural smectite, has been found to be a useful catalyst in a variety of organic reactions due to its strong acidity, inexpensive compared to ion exchange resin, noncorrosive, reusability and non-polluting [11–13]. Reactions catalyzed by montmorillonite clays are usually carried out at relatively mild conditions with high yield and selectivity towards the desired products [14]. Montmorillonite K10 is a type of acidic stratified silicate mineral with a three-layer structure. The ideal chemical formula is $(Al_{2-y}Mg_y)_2Si_4O_{10}(OH)_2 \cdot nH_2O$. It has great applications in organic transformation and has offered major breakthroughs to fine chemical manufacturing industries [15].

In its natural form, montmorillonite K10 clay contains Brønsted acid sites. However, it can be easily turned into a basic material by treating it with a basic cation-containing solutions such as K_2CO_3 [10], NaOH, KOH or LiOH [16,17]. Lithium-modified montmorillonite has been reported to have high concentration of lithium cations at loadings larger than those of other metal cations on a gram atom basis. Manoratne et al. [16] reported that the hydration power of Li^+ cations was high. Therefore, it could be assumed that Li^+ cations in the interlayer gallery would be hydrated, in addition to the weakly bonded water molecules within the layers. The intercalation of Li^+ ions within the interlayer spacing of montmorillonite has a significant effect on water uptake to make montmorillonite more hydrophilic [13]. However, the use of basic clay catalyst in glycerolysis can result in the excessive adsorption of glycerol to consequently result in reduced catalytic activity.

The use of aqueous alkali and phase transfer catalyst (PTC) in various organic reactions has been attempted recently. Aserin et al. [18] synthesized monoglyceride using a PTC to overcome the problem of low solubility of sodium stearate in epichlorohydrin. Over 90% of pure non-food grade monoglycerides was obtained in quantitative yields after short reaction times at a relatively low temperature. However, it should be highlighted that monoglycerides prepared through this method were not food grade products.

Bhatkhande et al. [19] reported that the presence of PTC was of prime importance in the saponification of vegetable oil using aqueous alkali. Lopez and Pleixats [20] described the treatment of sultam-derived N-(diphenylmethylene)glycinate with activated organic bromides and with Michael acceptors under solid–liquid PTC conditions. K_2CO_3 was used as the base catalyst and monoalkylated compounds with high diastereoselectivity (>97%) were obtained. Zhang et al. [21] found that base-catalyzed transesterification reaction rate could be enhanced with PTCs such as cetyltrimethylammonium bromide, tetrabutylammonium hydroxide and tetrabutylammonium acetate as indicated by high methyl ester content obtained after only 3 min of reaction. Maybodi et al. [22] also demonstrated that the overall time of oscillating reaction greatly decreased with an increase in the concentration of tetramethyl ammonium hydroxide (TMAOH) in a luminal– H_2O_2 – $KSCN$ – $CuSO_4$ –TMAOH system. In this case, the period of oscillation did not change considerably with the variation in the TMAOH concentration.

The use of basic clay in conjunction with PTC provides potential synergical effects of their properties and catalytic activity. Interaction between the surfactant with the surface of clay particles can influence the stability and the flow behavior of clay–water system [23]. When mixed with organic molecules, clay minerals present a proton rich environment. On the other hand, the catalytic abilities can be improved by providing organic cations in the interlamellar space which enables the accessibility of reactants. In this report, effects of calcination temperature on the characteristics and catalytic behaviors of LiOH-modified montmorillonite have been investigated. Further improvement in the reaction has been studied by the use of TMAOH with the objective of improving selectivity to

glycerol monolaurate. Focus is given to correlate the characteristics of the catalyst with their catalytic behaviors.

2. Experimental

2.1. Reagents and materials

Glycerol (99%), methyl laurate (ML, 98%) and montmorillonite K10 (MMT K10) used in this study were obtained from Fluka while lithium hydroxide (LiOH, 99.9%) and tetramethylammonium hydroxide (TMAOH, 99.9%) were purchased from Merck. All the above materials were used without further purification. Deionized water was used throughout this work.

2.2. Preparation of base modified montmorillonite

A 250 mL round bottom flask equipped with a reflux condenser was charged with 10 g of MMT K10, 100 mL of deionized water, and the desired amount of LiOH solution. This mixture was then stirred and heated under reflux condition for 6 h and the slurry was then allowed to cool down to room temperature. The resulting solid was then separated from liquid by centrifugation and the liquid portion was decanted and discarded. The wet solid was then washed by dispersing it in 500 mL of deionized water and the centrifugation step was repeated. The catalyst was then calcined in a furnace at 350, 450, 550, 650 °C for 4 h. The catalysts obtained are denoted as K10-MMT for the original montmorillonite material, and $LiK10_x$ for the LiOH-intercalated montmorillonite materials in which subscript 'x' represents the calcination temperature used.

2.3. Characterization of catalyst

Basic strength of the catalysts was determined using Hammett indicator method (H₊). About 25 mg of the catalyst samples were shaken with 5.0 mL of Hammett indicator solutions which had been diluted with methanol and left to equilibrate for 2 h [24]. After 2 h, the color of the catalysts was observed. The Hammett indicators used were neutral red (H₊ = 6.8), bromothymol blue (H₊ = 7.2), phenolphthalein (H₊ = 9.3), 2,4-dinitroaniline (H₊ = 15.0), and 4-nitroaniline (H₊ = 18.4).

FTIR spectra of sample-KBr pressed disk were obtained using a Perkin-Elmer 1725X Fourier transform infrared spectrometer. For each measurement, 0.9 mg of catalyst and 63 mg of potassium bromide (KBr) were weighted and then ground in an agate mortar for 10 min before pressing to form pellets. FTIR spectra were collected over the spectral range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1} .

2.4. Catalyst activity test and product sampling

Transesterification reaction of glycerol with methyl laurate (ML) was performed in a glass jacketed reactor which was equipped with a heated condenser system. The water circulation temperature of condenser was kept at 80 °C so that only methanol (reaction product) was allowed to escape from the reaction vessel. This was done to ensure the promotion of the forward reaction to selectively give glycerol monolaurate. Glycerol, methyl laurate and the clay catalyst were mixed under magnetic stirring and heated in a silicone bath to the required temperature without any solvent. After 5 h, 100 μ L of the reaction mixture was withdrawn from reaction vessel and put into sample vials containing 100 μ L of water and 100 μ L of methyl acetate, according to a method reported by Yang et al. [25]. The vials were then vortexed and the organic phase containing acylglycerols and fatty acid was separated by means of centrifugation. To this, 0.1 mL of 0.2 M internal standard and 0.5 mL of acetone were

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