Selective Glycerol Esterification Over Organomontmorillonite Catalysts

(Pengesteran Gliserol Terpilih Menggunakan Pemangkin Organomontmorilonit)

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ABSTRACT

Organomontmorillonites were synthesized by grafting cationic surfactants i.e quaternary ammonium compounds into the interlayer space and were characterized using XRD, FTIR and N_2 adsorption/ desorption analysis. The organomontmorillonites were applied as catalyst for the esterification of glycerol (GL) with lauric acid (LA). The catalyst which had symmetrical onium salts (tetrabuthylammoniumbromide, TBAB) gave higher activity than that of unsymmetrical onium salts (cetyltrimethylammoniumbromide, CTAB). Over the TBAB-montmorillonite catalyst, glycerol monolaurate was obtained with a selectivity of about 80%, a lauric acid conversion of about 71% and a glycerol monolaurate yield of about 57%.

Keywords: Esterification; lauric acid; monoglyceride; montmorillonite; reaction

ABSTRAK

Organomontmorilonit telah disintesis melalui percantuman surfaktan kation iaitu sebatian ammonia kuartener kepada ruang lapisan-antara dan dicirikan menggunakan analisis XRD, FTIR dan jerapan/penyahjerapan N_2. Organomontmorilonit ini telah digunakan sebagai mangkin bagi pengesteran gliserol (GL) dengan asid laurik (LA). Pemangkin yang mempunyai garam onium simetri (tertabutilammoniumbromida, TBAB) memberikan aktiviti yang lebih tinggi berbanding pemangkin yang mempunyai garam onium tak simetri (setiltrimetilammoniumbromida, CTAB). Melalui pemangkin TBAB-montmorilonit, gliserol monolaurat telah diperolehi dengan pemilihan sebanyak 80%, penukaran asid laurik sekitar 71% dan hasilan gliserol monolaurat sekitar 57%.

Kata kunci: Asid laurik; monogliserida; montmorilonit; pengesteran; tindak balas

INTRODUCTION

In the last decade, renewable raw materials have become very important in the search for a sustainable chemistry. Vegetable oils and fats are the largest source of renewable raw materials used in the chemical industry. The most important benefits from oleochemicals are their biodegradability and nontoxic characters, which allow the preparation of environmentally friendly surfactants.

Malaysia is the world's leading producer of palm oil. This industry promotes several downstream industries among which are oleochemical and biodiesel industries. The main reactions used in oleochemistry are the hydrolysis or the methanolysis of triglycerides leading to glycerol and fatty acids or fatty methyl esters. However, these reactions also lead to the formation of glycerol and there is an urgent need to find valuable applications for this low value side-product.

The glycerol transformation into glycerol monoesters (monoglycerides) has significant applications in food, pharmaceutical, cosmetics or in detergent chemistry (Lauridsen 1976). The monoglycerides are generally obtained from: (1) the glycerolysis of triglycerides, (2) the hydrolysis of triglycerides or (3) the direct esterification of glycerol with fatty acids (Figure 1). The current industrial processes for monoester production lead to blends of mono-, di- and even some tri-glycerides, and dissolved glycerol. These blends typically contain 40-60% monoglyceride, and 35-45% diglycerides. However, as the emulsifying properties of diesters are poor and the surface properties of the blends relies upon their monoester content. Therefore, for many applications, energy consuming vacuum molecular distillation has to be used to raise the monoglyceride content up to ~90%. Another drawback of current processes is the generation of waste chemicals due to the need to neutralise and remove the catalysts used in the reaction, either basic or acid.

A number of solid acids have been used as catalysts for the fatty acid esterification of glycerol in order to avoid the problems associated with the use of homogeneous catalysts. The development of alternative catalysts for the esterification, which have high activity, high productivity, and easy recovery without severe environmental pollution, is the emerging topics concerning the aspect of the green-chemical processes. Recently, some studies involving alternative heterogeneous catalytic routes have been reported such as the glycerol esterification with lauric and

FIGURE 1. Simplified chemical equation for fatty acid glycerolysis

oleic acids by using solid cationic resins (Abro et al. 1997), zeolitic molecular sieves (Heykants et al. 1997; Machado et al. 2000), sulfated iron oxide (Guner et al. 1996) and functionalised mesoporous materials (Bossaert et al. 1999) as catalysts.

Due to the unique surface properties such as surface acidity, cation exchange capacity and high surface areas, layered aluminosilicates, so called clays, have been widely investigated. Among the various layered aluminosilicates generally used as a host matrix, montmorillonite which is classified into 2:1 type dioctahedral smectites has received great attention because of its good swelling property and high exchange capacity.

Applications of cation-exchanged montmorillonites, pillared clays and clay-supported reagents have been extensively studied in organic synthesis under milder reaction conditions. Several functionalised organic polymers (Montanari et al. 1981) and mineral supports (Cornelis et al. 1983) have been used as triphase catalysts that contain immobilized organocations, such as quaternary ammonium ions analogues to those used for conventional liquid–liquid phase-transfer catalysts. Although triphase catalysis greatly simplifies the recovery of the catalyst and provides opportunities for selective chemical conversions based on substrate size or polarity, the system also has some limitations. Silica, alumina and polymers are unstable in strong acidic and alkaline media and have low physical strength. In comparison, clays are cheap, have high physical strength, and possess relatively high resistance towards alkali treatment. Some work has appeared on the use of clays as supports for quaternary salts (Lin &

Pinnavia 1991; Varma & Naicker 1998; Yadav & Naik, 2000). This prompted us to explore the use of immobilised onium cations pillared clays as catalysts in a nucleophilic substitution reaction.

This paper reports changes in the structure of a montmorillonitic clay which has been intercalated with a long-chain organic surfactant. X-ray diffraction and FTIR analyses have been used to study the changes in the type of surfactant -dependent organoclays. The objectives of the research are to study the change in structure of the organoclays with surfactant and to evaluate the capability of organomontmorillonite as catalysts for the selective esterification of lauric acid and glycerol into monoglyceride. We also compared the activity and selectivity obtained on various organomontmorillonite.

EXPERIMENTAL

MATERIALS

The montmorillonite used in this study as source clay, Na-montmorillonite (Na-MMT) clay with cation exchange capacity (CEC) of 119 meq/100 g, was supplied by Kunimine Industry Co., Japan. The surfactant used in this study were cetyl trimethyl ammonium bromide (CTAB, $C_{19}H_{42}BrN$, FW: 364.448) from Fisher Scientific and tetra-n-butylammonium bromide (TBAB, $C_{16}H_{36}BrN$, FW: 322.368) from Sigma Aldrich. Lauric acid (Fisher) and glycerol (Fisher) with a purity of 99% were used in this study without purification.

PREPARATION OF ORGANOMONTMORILLONITE CATALYSTS

The synthesis of organomontmorillonite was undertaken by the following procedure. Na-montmorillonite (5 g) was first dispersed in 400 mL of distilled water under stirring with a Heidolph magnetic stirrer at about 600 rpm for about 20 h. A predissolved stoichiometric amount of cetyl trimethyl ammonium bromide (CTAB) or tetra-n-butylammonium bromide (TBAB) solution was slowly added to the clay suspension at 60°C. The reaction mixtures were stirred for 60 min at 60°C using a Branson Ultrasonics Model 250 sonifier with an output of 40 W. The acoustic wave was introduced directly into the sample solution through a standard titanium horn. All organoclay products were washed free of bromide anions as determined by the use of AgNO$_3$, dried at room temperature, ground in an agate mortar, screened with a 200-mesh sieve and stored in a bottle glass.

CHARACTERIZATION OF ORGANOMONTMORILLONITE CATALYSTS

The Na-montmorillonite and organomontmorillonite were pressed in stainless steel sample holders. X-ray diffraction (XRD) patterns were recorded using CuKα radiation on a Bruker Advance X-ray Solution diffractometer operating at 40 kV and 40 mA between 3 and 10° (2θ) at a step size of 0.0514°. The corresponding d spacing can be calculated from the Bragg equation: d = λ/(2 sin θ) where λ is the wavelength of X-ray (λ = 1.5418Å).

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

The surface area measurements were made on an ASAP 2010 apparatus (Micromeritics). N$_2$ and Ar adsorption/ desorption isotherms were performed at 77 and 87 K, respectively, in an after pretreating the samples under vacuum at 673 K overnight and the surfaces were obtained using the BET methodology.

CATALYST TEST

The esterification of glycerol with fatty acids was accomplished directly in the liquid phase (without solvent), in a stirred flask heated in an oil bath under atmospheric pressure. The reaction temperature was 130°C. The amount of catalyst, previously dried at 100°C overnight, used was 2.5 wt. %. The molar ratio of glycerol:fatty acid was 6. The TG, DG, MG, and FA contents in the reaction product were analysed using a gas chromatograph (GC).

For the product analysis, 100 μL of sample was withdrawn from reaction vessels at various intervals and put into a sample vial containing 100 μL of water and 100 μL of methyl acetate. The solutions were 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 of internal standard and 0.5 mL of acetone0 were added, and then 10 μL of the sample was injected into the GC. The composition was analysed on a Hwlet Packard 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. x 0.1 μm df). The temperatures of the injector and detector were set at 250 and 380°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 and maintained at 330°C for 3 min. The split ratio was 1:5. The degree of esterification was expressed as the ratio of the amount of FA consumed in the reaction to the initial amount of FA before the reaction. The MG and DG contents were expressed as the sum of the wt % of their regioisomers. The authentic standards of TG, DG, MG, and FA were additionally used for identification.

RESULTS AND DISCUSSION

X-RAY DIFFRACTION

With the cation exchange of the sodium ion for the cationic surfactant, expansion of the montmorillonitic clay layers occurred. This expansion was readily measured by X-ray diffraction. Figure 2 shows the XRD patterns of Na-montmorillonite and organomontmorillonite at different surfactant (cetyl trimethyl ammonium montmorillonite, CTMMT and tetra-n-butylammonium montmorillonite, TBMMT). Figure 2 clearly shows the increase in the d-spacing from 11.1 to >16.0 Å. The graph also shows that for CTMMT, the d-spacing is larger than that of TBMMT (19.4 and 16.8 Å, respectively). This could be related to the molecular structure and size of intercelated species. CTAB has a long alkyl group (cetyl) in comparison with TBAB which have only butyl groups. These results show that replacing the sodium ions with large ammonium cations resulted in an increase in the d-spacings. In addition, larger substituents on the ammonium ion led to higher d-spacings (lower 2θ angles) for the organoclay. In other words, the montmorillonite gallery expanded as needed to accommodate more intercalated material.

FTIR

In order to obtain complementary evidence for the intercalation of quaternary alkylammonium cations into the silicate lattice, FT-IR spectra were recorded in the region of 400 – 4000 cm^{-1}. Figure 3 shows the IR spectra of NaMMT and its alkylammonium derivatives. An intense relatively sharp band was observed at 3,630 cm^{-1}. The band was affected by the presence of quaternary cation and was assigned to the OH-streching vibration of montmorillonite clay. A pair of strong bands near 2,850 and 2,930 cm^{-1} at the both organomontmorillonite spectrum could be assigned to the symmetric and asymmetric stretching vibrations of the metylene group (γ_{CH2}) of the guest molecules (Li & Ishida
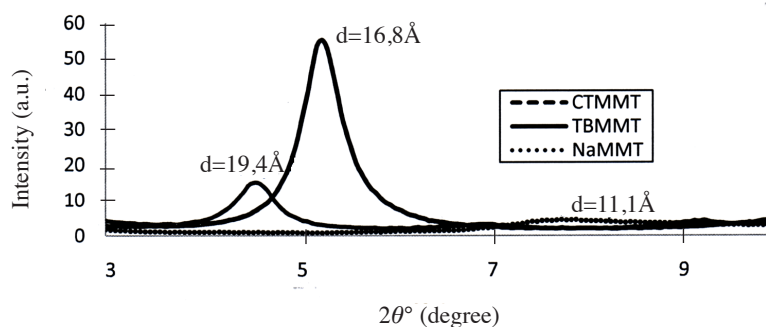
FIGURE 2. X-ray diffraction pattern of Na-MMT and organomontmorillonite
hybrids (CTMMT and TBMMT)

2003). In the case of CTMMT and TBMMT, including the ester group, a strong absorption band at 1,640 cm⁻¹ due to the stretching vibration of the carbonyl (-C-C= O-) group was observed, supporting the intercalation of surfactant molecules between the silicate layers. The band of the surfactant modified clay at 1,475 cm⁻¹ shows significant changes in the methyl deformation region. The methyl groups were probably linked into the siloxane surface (Faridi & Guggenheim 1997). The infrared band, observed at 1,037 cm⁻¹, for the untreated montmorillonite shows a shift in band position upon immediate contact with the CTAB or TBAB surfactant. The significance of these results rests with the interaction between the surfactant molecules and the siloxane surface. These results shows that there was an interaction between the surfactant molecule and the montmorillonite siloxane layer immediately upon contact (Xi et al. 2005).

SURFACE ANALYSIS

Table 1 presents the specific surface area, average pore diameter and pore volume of catalyst. Surface area of raw NaMMT was found to be ~24 m²/g. The size of the organic cation and the clay layer charge affect the surface area and pore structure of the organoclays and hence their adsorption efficiencies. The surface area of organoclay decreased as the size of organic cation increased. It is obvious that the micropores were substantially diminished by the surfactant adsorption, especially in the case of CTMMT. This explains why its specific surface area decreased more than in the case of TBMMT. According to Barrer (1989), in the ammonium cations play the role of pillar these organoclays. It held the layers permanently apart without filling all the interlayer space, thus preserving the distance between the layers.
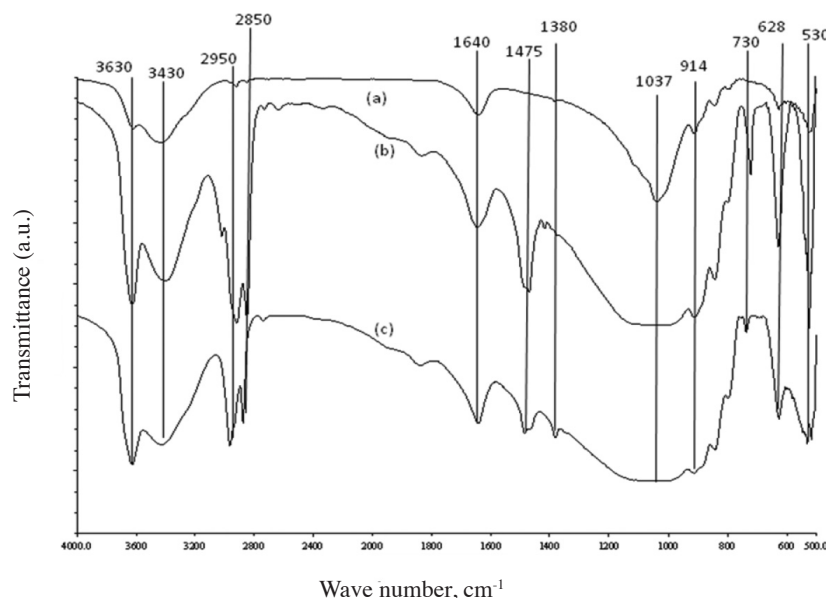

FIGURE 3. Infrared spectra of pristine (a) NaMMT and its quarternary alkylammonium
derivatives; (b) CTMMT, (c) TBMMT

TABLE 1. Surface characteristics of the organoclay catalysts

Sample	BET surface area, m²/g	Average pore diameter, Å	Pore volume, cm³/g
NaMMT	23.59	41.41	0.0391
TBMMT	10.96	140.33	0.0484
CTMMT	1.52	203.99	0.0115

CATALYST TEST

The mechanisms of clay–supported phase transfer catalyst (PTC) depend on whether the support is wetted by the aqueous phase or organic phase or is of mixed-wet type. Under a dynamic situation, a strongly water-wet system always retains a thin film of water around the particle. The organic phase does not penetrate inside the pores of the catalyst. Thus, the catalytic action is limited to the exterior surface of the support. The clay-particles were coated with the quaternary salt. The organic phase was the continuous phase, and the aqueous phase the dispersed phase (Yadav & Naik 2000).

The wettability of the clay containing quaternary salt as a solid occupying the pores is water-wet. Typically, the aqueous phase droplet, would stick to the clay-exterior surface upon intense agitation and exchange the nucleophile with the leaving group attached to the clay, C~, where C stands for clay. Lin and Pinnavia (1991) have commented about the type of bonding between quaternary salts and clay supports. The bonding between the quaternary salt and clay is totally by electrostatic but strong enough, and the (CTAB/TBAB) has very limited solubility in either aqueous or organic phase.

In general, Choy et al. (1997) found that an onium salt must have the proper hydrophobic-hydrophilic balance to be an efficient PTC. This balance is generally found when the total number of carbon atoms about the nitrogen atom is in the range of C_{16}–C_{20}. Below this range the partition coefficient of the onium salt favors the aqueous phase, whereas much above this range (e.g., tetradecylammonium bromide) emulsification problems complicate the reaction procedure. An additional factor affecting PTC activity is the structure of the onium salt catalyst. Symmetrical onium salts are generally more efficient PTC than the unsymmetrical onium salts with approximately the same car bon number (compare TBAB with CTAB).

We have studied the effect of catalyst structure on the reaction rate for ammonium salts-CTAB, and TBAB, each with 5 wt% ratio to the lauric acid. The reaction profile for each of these catalysts is presented in Figure 4. It shows that the catalyst which had symmetrical onium salts (TBAB) was more efficient in the catalytic process.

Figure 5 compares the selectivity to glycerol monolaurate for different clay as well as for the blank reaction as a function of the total yield to monolaurate. The selectivity was quite more evident when TBMMT was used as the catalysts for the glycerol esterification, particularly the former, producing larger quantities of monoglycerides than CTMMT or NaMMT at similar conversions. These results probably were the consequence of the hydrophobicity

and surface area exhibited by TBMMT, which were more adequate for reactions involving the entry and outlet of big molecules throughout the clay channels.
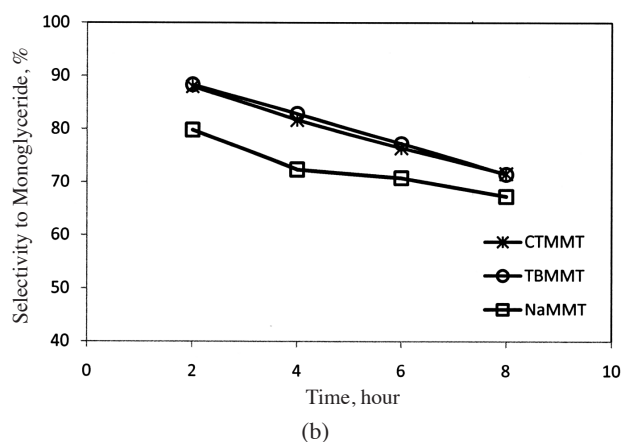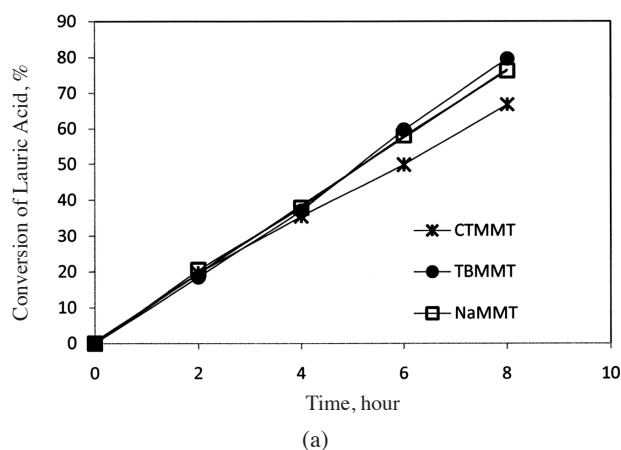

FIGURE 4. Variation of lauric acid conversion versus reaction time (a) and selectivity of monoglyceride versus reaction time (b). (Conditions: 403 K, glycerol/lauric acid molar ratio 6 and 5 wt. % catalyst)

CONCLUSIONS

The basal spacing obtained from X-ray diffraction give details of arrangement of surfactant in the organoclays. The catalyst which has symmetrical onium salts (tetrabuthyl ammonium bromide, TBAB) gave higher activity and selectivity than that of unsymmetrical onium salts (cetyltrimethyl ammonium bromide, CTAB). Over the TBAB-montmorillonite catalyst, glycerol monolaurate was obtained with selectivity of about 80% and conversion of lauric acid of about 71%. The results obtained using TBAB-
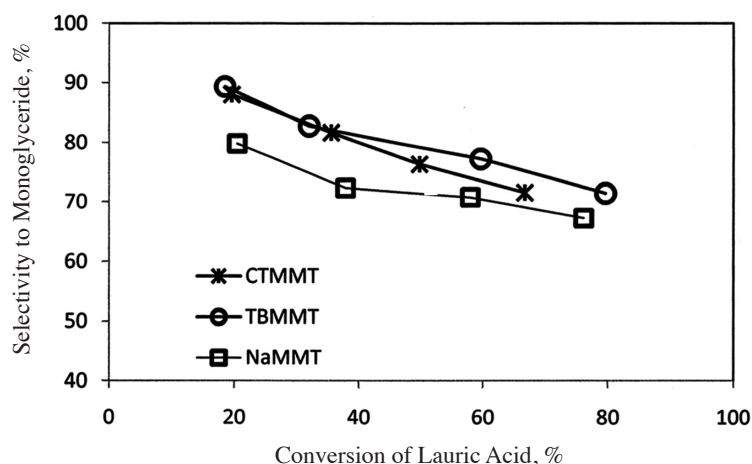
FIGURE 5. Conversion of lauric acid versus selectivity to monoglyceride.
(Conditions: 403 K, glycerol/lauric acid molar ratio 6, 5 % wt catalyst)

montmorillonite as esterification catalyst suggested that this material would be a potential candidate to replace the conventional non-selective homogeneous catalysts used for the synthesis of monoglycerides.

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