Comparison Studies on Lauric Acid Ethoxylated Using Homogenous and Heterogenous Catalysts

(Kajian Perbandingan Terhadap Asid Laurik Teretoksi Menggunakan Mangkin Homogen dan Heterogen)

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ABSTRACT

The application of homogenous and heterogeneous catalysts for ethoxylation of lauric acid (LAc) with ethylene oxide (EO) was conducted in this study. Ethoxylation reaction of LAc with EO with the mole ratio 1:3 (LAc:EO) have been done at reaction temperature 130-135°C under 1.8 bar pressure to produce Ethoxylated Lauric Acid (LAc:3EO), a type of nonionic surfactant. This experiment showed that potassium tert-butoxide (^{t}BuOK) as a base homogenous catalyst gave good selectivity and activity compared with potassium methoxide, potassium ethoxide and potassium butoxide. Studies on intercalation of hydrotalcite (HT) with ^{t}BuO$^-$ to form HT^{t}BuO as solid base catalyst was conducted. Ethoxylation reaction using heterogenous catalyst based on intercalated of HT-tBuO gave lower activity compared with ^{t}BuOK as homogenous catalyst. This might be due to diffusion which occurred significantly in heterogenous catalyst compared with homogenous catalyst. Analysis of nonionic surfactant LAc:3EO using HT^{t}BuO as a catalyst gave no undesired side product. Detail analysis of the reaction products using GC-Tof technique gave a mixture of ester of LAc:3EO and polyethylene glycol (PEG).

Keywords: Ethoxylated lauric acid; hydrotalcite; intercalation; nonionic surfactant tert-butoxide

ABSTRAK

Aplikasi mangkin homogen dan heterogen bagi tindak balas asid laurik (LAc) dengan etilena oksida (EO) telah dikaji. Tindak balas LAc dengan EO dengan nisbah molar 1:3 (LAc:EO) telah berjaya dilakukan pada suhu tindak balas 130-135°C di bawah tekanan 1.8 bar bagi menghasilkan asid laurik teretoksilat (LAc:3EO), sejenis surfaktan bukan ion. Eksperimen ini menunjukkan bahawa penggunaan kalium tert-butoksida sebagai mangkin homogen memberikan selektiviti dan aktiviti yang lebih baik berbanding kalium metoksida, kalium etoksida dan kalium butoksida. Kajian seterusnya dilakukan dengan menyelit anion ^{t}BuO$^-$ pada HT bagi menghasilkan mangkin bes pepejal HT^{t}BuO. Penggunaan mangkin heterogen HT^{t}BuO dalam tindak balas pengetoksilan memberikan aktiviti yang lebih rendah berbanding ^{t}BuOK sebagai mangkin homogen. Keadaan ini kemungkinan besar disebabkan oleh fenomena penyerakkan yang berlaku secara signifikan dalam mangkin heterogen berbanding dengan mangkin homogen. Hasil analisis GC-Tof terhadap surfaktan bukan ion AL:3EO yang menggunakan mangkin HT^{t}BuO menunjukkan kehadiran campuran ester dan polietilena glikol (PEG).

Kata kunci: Asid laurik teretoksilat; hidrotalsit; penyelitan; surfaktan bukan ion tert-butoksida

INTRODUCTION

Anionic clays, particularly hydrotalcites are a class of layered materials of current interest. It contains positively charge-balancing anions in the interlamellar space besides water molecules. Hydrotalcites are represented by the general formula $M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}[A^{n-}_{x/n}]^{x-}$, where M^{2+} and M^{3+} are bi- and trivalent metal cations such as Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Al^{3+}, Fe^{3+}, Cr^{3+}, respectively, and A is an interlamellar anion with charge n- such as Cl$^-$, NO$_3^-$, CO$_3^{2-}$ or any macrocyclic multivalent anions, etc., and x=0.1-0.33 (Cavani et al. 1991; Labajos et al. 1992). The exchangeable and inserting various anions into interlayers (intercalation) can give hydrotalcite new functions. Hydrotalcite are excellent materials as precursors of catalyst and have attracted much attention during the development of new environmentally friendly catalysts (Bolognini et al. 2002). Hydrotalcite-derived mixed oxides are well known for their potential application as ion exchangers, adsorbents and catalyst supports because of their high surface area and basic surface properties. In the present paper, we report the preparation and intercalation of hydrotalcite-like structure containing Mg, Al and tert-butoxide in the hydroxide layer for use as heterogeneous catalyst in ethoxylation of lauric acid. The Mg/Al molar ratio of 3.0 was chosen corresponding to reports from other researchers that maximum of the basic site density was observed at this ratio (Fishel & Davis 1994; Nakasuka et al. 1979; Xie et al. 2005).

Material and Methods

Material preparation

The hydrotalcites were prepared by coprecipitation method at low supersaturation method (Hreczuch & Szymanowski 1996). An hydrotalcite Mg-Al (ratio 3:1) containing carbonate as interlayer anion was synthesized by a modified coprecipitation method as described elsewhere (Xie et al. 2005). In this method, magnesium nitrate hexahydrate (30.8 g, 0.12 mole) and aluminium nitrate monohydrate (15.0 g, 0.04 moles) were dissolved in 100 mL deionised water. The pH of the solution was adjusted to 10 by the addition of NaOH (2 M). The slurry was stirred for 2 hour under nitrogen at room temperature, then filtered under nitrogen and dried under vacuum at 80°C. For intercalation, HT-tBuO was prepared from calcined HT (1.214 g) by ion-exchange with 0.1 M solution of potassium tert-butoxide in 100 mL THF with stirring, at room temperature for 24 hour. The precipitate (HT^{t}BuO) was filtered under nitrogen atmosphere to yield 1.382 g. This catalyst was used in ethoxylation reaction of LAc with EO with mole ratio of 1:3 (LAc:EO). The reaction was carried out between 130 and 135°C under a pressure of 1.8 bar to produce ethoxylated lauric acid (LAc:3EO), a type of nonionic surfactant.

Characterisation

The crystal structures of the hydrotalcite and intercalated hydrotalcite were examined by X-ray powder diffractometer and the patterns were recorded with a Philips model 1710 semiautomatic X-ray diffractometer with auto divergent slit and graphite monochromator using Cu K$_\alpha$ radiation at a scanning speed of 2°/min, operated at 40 kV and 20 mA. FTIR spectra of the samples were recorded from 180 to 4000 cm^{-1} in KBr phase with a Perkin Elmer FTIR spectrophotometer. TG/DTA of the samples were carried out in nitrogen atmosphere 50mL/min using a Mettler Toledo at a heating rate 10°C/min in the temperature 30-900°C. Specific surface area, pore volume, average pore diameter and pore size distribution were determined by nitrogen adsorption-desorption at liquid nitrogen temperature (-196°) using a ASAP 2010 (Micromeritics) instrument. Prior to adsorption-desorption analysis, the samples were equilibrated by degassing at 110°C and 10^{-4} Torr for 6 h to evacuate the physically adsorbed moisture.

Catalytic ethoxylation reaction was carried out in a special stainless steel reactor (1L) (Vinci Technologies) with stirrer and heating jacket outside the reactor. The catalyst and lauric acid were placed inside the reactor and flow by nitrogen gas for 5-10 minutes. The temperature was increased slowly to the desired temperature. After the temperature was stabilized, the reactor was vacuumed before the ethylene oxide was injected. The reaction occured for about 3 h. The product was collected and analyzed by GC and GC-Tof. In this paper, we have selected the homogenous and heterogeneous catalyst in various percents to compare the conversion of the product.

Results and Discussion

The XRD pattern of the 450°C calcined sample (Figure 1) showed sharp and symmetric peaks which gives clear indication that the samples are well crystallized and the peaks corresponding to (003), (006) and (009) planes are characteristic of clay mineral (hydrotalcite) having layered structure (Miyata 1983). The ^{t}BuO$^-$ has been well intercalated between HT interlayer as shown by shifting of (003) of the HT^{t}BuO 10.14° to 10.50° and showed that it was very crystalline. It can be observed clearly from SEM image (Figure 2) that HT has thin flat crystal. After intercalation, the structure of HT changed to form a crystal rod.

The IR spectra of hydrotalcite samples (Figure 3) showed an intense broadband between 4000 and 3000 cm^{-1} corresponding to the stretching vibrations of the hydroxyl groups of both the layer hydroxide moieties and interlayer water (Zhang et al. 2004). The broadening of this band is due to hydrogen bond formation (Rives 2001). A band close to 1629 cm^{-1} corresponds to the deformation mode (δH_2O) of water molecules. The intense band at 1383 cm^{-1} is attributed to the CO_3^{2-} absorption and the impurities of NO^{-3} which may be the result from the synthesis solution (Rey et al. 1992), whilst bands around 451-791 cm^{-1} are due
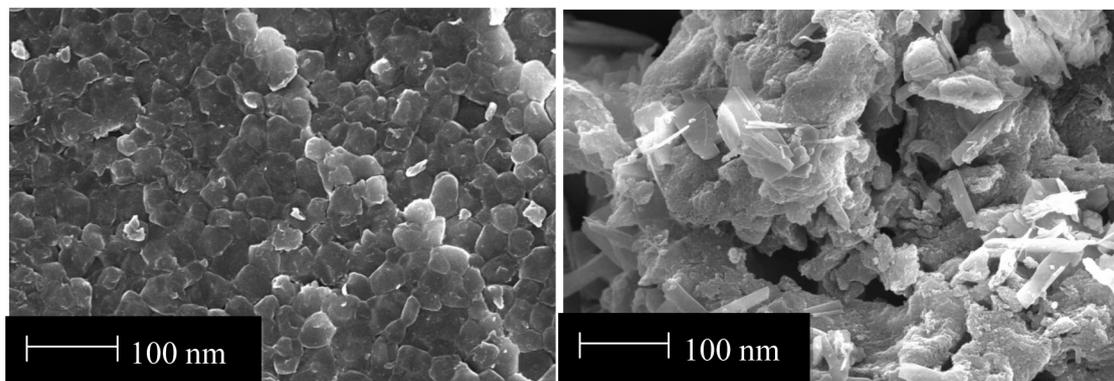

FIGURE 2. Scanning electron micrographs of HT (before intercalate) and HT-tBuO (after intercalated)
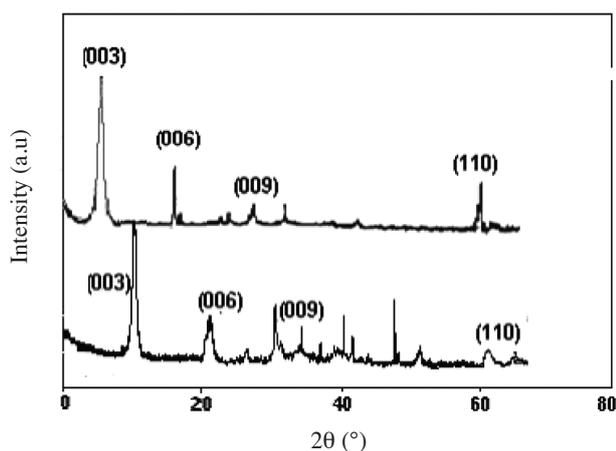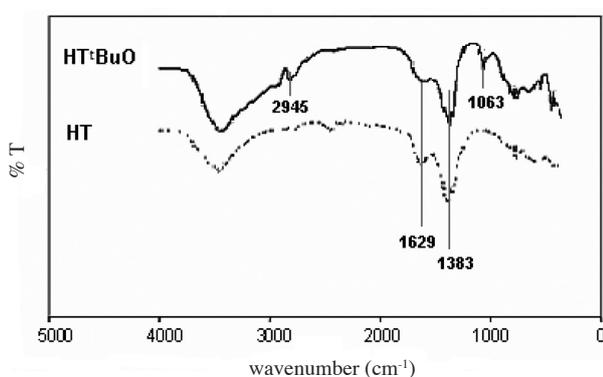
FIGURE 1. XRD pattern of HT and HT-tBuO

FIGURE 3. FTIR spectra of HT and HT-tBuO

to Al-O and Mg-O lattice vibrations, respectively (Rives 2001).

After intercalations with ^{t}BuO$^-$, the doublet around 791-656 cm^{-1} decreaced significantly in intensity of water and carbonate characteristic peaks due to the removal of water and CO_2 vapors during the calcinations and ion exchange (Parida & Das 1999). The main out-of-plane stretching vibrations of the C-H bonds (2945 cm^{-1}) and the absorption bands of the C-C-O (1063 cm^{-1}) in the spectrum of HT-tBuO, we assume that t-BuO$^-$ anions are intercalated.

The nitrogen adsorption/desorption behavior of HT and HT^{t}BuO is reported. In both cases, the nitrogen sorption follows an isotherm of type IV. As shown in Table 1, HT^{t}BuO as a potential catalyst posses a rather high surface area, 231 (m^2/g). Increase in the surface area is observed after the intercalation of ^{t}BuO$^-$ anions in the interlayer of HT.

Figure 4 shows that the thermal stability of ^{t}BuO$^-$ anion intercalated in HT is lower by three weight losses between 30 and 175°C (11.40%). This is due to water desorption. The second between 175-390°C (8.46%) is due to bound water adsorption and the third between 390-600°C (25.44%) is due to decomposition of ^{t}BuOH and remanding CO_3^- ion.

TABLE 1. Textural properties of HT and HT^{t}BuO

Sample	S_{BET} (m^2/g)	Average pore diameter (nm)
HT	193	13.8
HT^{t}BuO	231	12.3

The catalytic performances of the various materials for the synthesis of ethoxylation lauric acid are represented in Figure 4. The activity of the new catalysis, HT^{t}BuO is compared to that the HT and homogenous catalyst, potassium tert-butoxide (^{t}BuOK). The percentage of product for all catalysts increased by increasing percent of catalysts. Ethoxylation reaction using homogenous catalyst, ^{t}BuOK gave more than 90% w/w product compared with heterogeneous catalyst HT^{t}BuO which produce only 65% w/w product. Different in this percent yield might be due to some diffusion factor which might occurs from ^{t}BuO$^-$ which was trapped in the HT interlayer and react with EO. Meanwhile, the 1%-1.5% of HT-calcined showed no further conversion of EO.
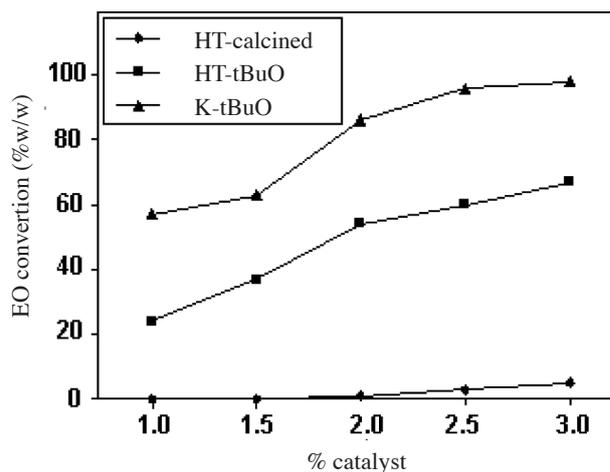

FIGURE 4. Catalytic activity of HT-calcined, HT ^{t}BuO and ^{t}BuOK in various percemt catalysts on ethoxylation of lauric acid

GCxGC-ToF analysis of product showed that oligomers of ester and polyethylene glycol product was obtained as shown in Table 2. GC-ToF chromatogram shows that the molecular structure after the ethoxylation reaction gives many oligomers product compared with the expected product (LAc:3EO) as shown in Figure 5. Eight major peaks were determined as oligomers of ester and polyethylene glycol group were identified.

CONCLUSION

Intercalated hydrotalcite Mg-Al with ^{t}BuO$^-$ was done by ion exchange process of Mg-Al carbonate to tert-butoxide (^{t}BuO$^-$) for 24 h. XRD analysis of intercalated HT^{t}BuO showed that ^{t}BuO$^-$ has been intercalated well

TABLE 2. Data collected in GCxGC-ToF result for LAc:3EO product

| Retention time (min)	Molecular weight	Formula	Compounds	Label
7.61	106	$C_4H_{10}O_3$	Diethylene glycol	PEG2
9.36	244	$C_{14}H_{28}O_3$	Ethylene monolauryl ester	AL-1EO
10.33	231	$C_{26}H_{30}O_4$	Ethylene lauryl diester	Diester 1EO
11.77	288	$C_{16}H_{32}O_4$	Diethylene monolauryl ester	AL-2EO
13.19	194	$C_8H_{18}O_5$	Tetraethylene glycol	PEG4
14.90	319	$C_{28}H_{34}O_5$	Triethylene lauryl diester	Diester 3EO
15.86	322	$C_{18}H_{36}O_5$	Triethylene monolauryl ester	AL-3EO
17.18	420	$C_{20}H_{40}O_6$	Tetraethylene monolauryyl ester	AL-4EO
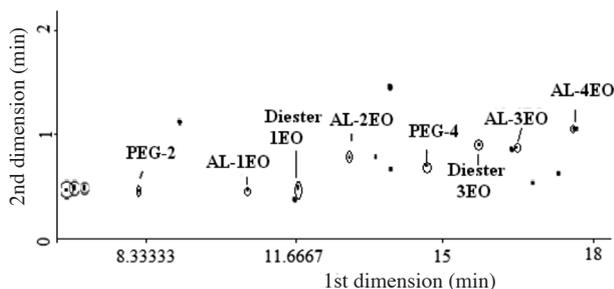
FIGURE 5. GC-ToF chromatogram shows the product in LAc:3EO

between hydrotalcite interlayer as shown by shifting of 2θ (10.14 Å to 10.50 Å). By comparing homogenous catalyst, potassium tert-butoxide gave more than 90% w/w product than heterogeneous catalyst which produced only 65% w/w product. Difference in percent yield was due to some diffusion factors that occurred for $^tBuO^-$ which was trapped in the hydrotalcite interlayer and react with EO. Even though the reported conversions were low and thus are not of practical value, the use of this heterogeneous catalyst is advantageous because of its easy separation from the product. Analysis by GCxGC-ToF technique showed that this product contains oligomer of LAc-3EO and polyethylene glycol (PEG) namely ethylene monolauryl ester, diethylene monolauryl ester, triethylene monolauryl ester, tetraethylene ester, diethylene glycol, triethylene glycol, tetraethylene glycol and pentaethylene glycol.

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