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Biodiesel production from soybean oil using calcined Li–Al layered double hydroxide catalysts

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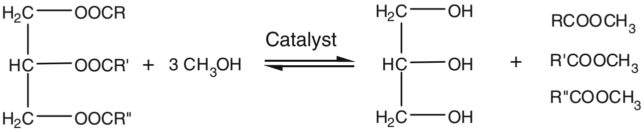
The transesterification of soybean oil to fatty acid methyl esters was studied using a calcined Li–Al layered double hydroxide catalyst. The catalyst exhibited high activity, with near quantitative oil conversion being obtained under mild conditions (reflux temperature of methanol) and short reaction times (≤ 4 h). The influence of relevant parameters (catalyst calcination temperature, methanol to oil mole ratio, catalyst charge and reaction duration) was examined.

KEY WORDS: biodiesel; transesterification; layered double hydroxide; lithium; aluminum.

1. Introduction

Low-cost, high capacity processes for the conversion of biomass into fuels and chemicals are essential for expanding the utilization of carbon neutral processes, reducing dependency on fossil fuel resources, and increasing rural income. One immediate solution for reducing petroleum consumption is the use of biodiesel blends as transportation fuels. Commercially, biodiesel is produced from edible vegetable oils, including rapeseed, sunflower and soybean oil, as well as animal fats. These oils and fats are typically composed of C_{14}–C_{20} fatty acid triglycerides (constituting ~90%–95% of the oil by weight). In order to produce a fuel that is suitable for use in diesel engines, the triglycerides are converted to the respective alkyl esters and glycerol by transesterification with short chain alcohols, typically methanol [1]:



In addition to being used as biodiesel, the resulting fatty acid esters are widely used in the synthesis of lubricants, surfactants, oleochemicals and polymers. The glycerol co-product has applications in the pharmaceutical, cosmetics, food and plastics industries.

Transesterification can be catalyzed by both acids and bases. Industrially, homogeneous base catalysts are used, including sodium or potassium hydroxides or alkoxides. Base catalysis is preferred to the use of acid catalysts such as sulfuric or sulfonic acids, given the corrosivity and lower activity of the latter. However, removal of the base after reaction is problematical, since the current practice of aqueous quenching with acid results in some degree of saponification (i.e., hydrolysis of the esters and formation of the corresponding metal carboxylates), as well as the formation of emulsions which render separation of the fatty acid esters difficult [1]. Further, an alkaline waste water stream is generated.

In order to circumvent these problems, the use of heterogeneous catalysts has been explored. This approach eliminates the need for an aqueous quench and largely eliminates the formation of metal salts, thereby simplifying downstream separation steps; consequently, biodiesel production can be more readily performed as a continuous process. Based on their ready availability, solid acid catalysts such as zeolites, clays and ion exchange resins are attractive for this purpose, however, reaction rates are generally found to be unacceptably low. Consequently, solid base catalysts have attracted attention. Catalysts of this type include simple metal oxides such as MgO and CaO in supported or unsupported form [2–4], Zn–Al mixed oxides [5, 6], cesium-exchanged zeolite X [4], anion exchange resins [2], polymer-supported guanidines [7], Na/NaOH/Al_2O_3 [8], and K- and Li-promoted oxides, prepared by impregnating the corresponding nitrate or halide salt onto an oxidic carrier such as Al_2O_3 [9, 10], ZnO [11] or CaO [12].

Additionally, layered double hydroxides (LDHs) have attracted interest for vegetable oil transesterification. LDHs are lamellar mixed hydroxides, the mineral hydrotalcite, $[Mg_{0.75}Al_{0.25}(OH)_2](CO_3)_{0.125} \cdot 0.5H_2O$, being the most well known example. LDHs possess a

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number of properties which should render them efficient catalysts for this purpose, including tunable basicity (via modification of the chemical composition) and high surface area. Upon heating, LDHs decompose to mixed oxides with loss of water and CO_2 (for the carbonate form of the LDH). The mixed oxides are of particular interest due to their increased basicity relative to the precursor LDHs, increased surface area (up to ~300 m^2/g) and homogeneous mixing of the different elements [13]. Indeed, several recent studies [14–17] have shown that calcined Mg–Al LDHs possess moderate activity in transesterification reactions. Further, Corma and co-workers [16] have reported that calcined Li–Al and Mg–Al LDHs are able to catalyze the glycerolysis of fatty acid methyl esters to monoglycerides (the reverse of biodiesel synthesis). The Li–Al catalyst was reported to be more active than the Mg–Al material (or MgO) due its higher Lewis basicity. This result suggests that calcined Li–Al LDHs should likewise be effective catalysts for biodiesel synthesis from vegetable oils, prompting the following study.

2. Experimental

2.1. Catalyst preparation

$[Mg_{0.73}Al_{0.27}(OH)_2](CO_3)_{0.135} \cdot mH_2O$ was prepared according to the method of Reichle [18]. A solution of $Al(NO_3)_3 \cdot 9H_2O$ (37.5 g, 0.1 mol) and $Mg(NO_3)_2 6H_2O$ (76.9 g, 0.3 mol) in 210 ml deionized water was added dropwise at room temperature to a mixture of NaOH (36 g, 0.9 mol) and Na_2CO_3 (30 g, 0.28 mol) in 330 ml of deionized water. Vigorous stirring was maintained throughout the ~60 min addition period. The resulting precipitate was left to age in the reaction mixture under gentle stirring at 75 °C overnight and was subsequently isolated by a cycle of centrifuging/decanting/washing with deionized water until the washings attained a pH of 7. The resulting solid was dried at 60 °C in a vacuum oven. The measured residual sodium content was 157 ppm.

$[Al_2Li(OH)_6](CO_3)_{0.5} \cdot mH_2O$ was prepared following the method of Sissoko *et al.* [19]. A solution of $Al(NO_3)_3 \cdot 9H_2O$ (37.5 g, 0.1 mol) in 250 ml deionized water was added dropwise at room temperature to a mixture of $LiOH \cdot H_2O$ (78.3 g, 0.9 mol) and Na_2CO_3 (5.1 g, 0.048 mol) in water (600 ml). Vigorous stirring was maintained throughout the ~60 min addition period. The resulting precipitate was left to age in the reaction mixture under gentle stirring at 75 °C overnight and isolated as described above. The measured lithium and aluminum contents were 2.01 and 33.54wt%, respectively. Additionally, a residual Na content of 34 ppm was measured. It should be noted that analyses of the filtered reaction mixtures from the transesterification experiments (see 2.3 below) indicated the absence of dissolved sodium (0.1 ppm detection limit), showing that leaching of Na^+ from the Li–Al catalyst does not occur under the reaction conditions (and hence does not contribute to the observed catalytic activity).

To produce mixed oxides, the layered double hydroxides were calcined in air at 450 °C for 2 h unless otherwise indicated. The resulting mixed oxides were stored in a vacuum dessicator.

The preparation of Li-promoted Al_2O_3 was accomplished by incipient wetness impregnation of γ-Al_2O_3 (Sasol, 217 m^2/g) with aqueous LiOH, to give a 2wt% Li loading. The solid was dried in a vacuum oven at 60 °C and then calcined in air at 500 °C for 3 h.

2.2. Characterization methods

Surface area and pore volume measurements were performed according to the BET method by nitrogen adsorption at −196 °C using a Micromeritics Tri-Star system. Catalyst samples were outgassed overnight at 160 °C under vacuum prior to the measurements. The chemical composition of the catalysts was determined using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). Powder X-ray diffraction (XRD) measurements were performed on a Phillips X'Pert diffractomer using Cu K_α radiation ($\lambda = 1.5406$ Å) and a step size of 0.02°. Peak simulation was performed using a standard fitting program [20]. Average crystallite sizes were calculated using Fourier integral breadth analysis. Weight loss on thermal treatment was determined using a Thermal Analysis TGA system. Samples were heated in a flow of air at 10 °C/min from room temperature to 800 °C.

The basic strength of the catalysts was determined using Hammett indicators, according to literature protocols [10]. The Hammett indicators used were neutral red ($pK_a = 6.8$), phenolphthalein ($pK_a = \sim 9.3$), Nile blue ($pK_a = 10.1$), 2,4-dinitroaniline ($pK_a = 15$) and 4-chloro-2-nitroaniline ($pK_a = 17.2$). Methanol was used as the solvent. When a color change of the indicator was observed, the H_ value of the basic sites was taken to be higher than the pK_a value of the indicator.

2.3. Transesterification of soybean oil

A total of 15.0 g of soybean oil (Spectrum Naturals, expeller pressed organic soy oil, acid value of < 0.1 mg KOH/g, 0.02% water by Karl Fisher titration) was weighed into a 100 ml two-neck reaction flask. Anhydrous methanol (Aldrich, < 0.002% water, 6:1–40:1 MeOH:oil mole ratio) was added to the flask. The mixture was stirred vigorously and heated to reflux temperature (65 °C), whereupon the appropriate amount of catalyst (1–3wt% relative to vegetable oil) was added. The reaction was allowed to proceed for a specified amount of time (1–6 h), after which the mixture was filtered and methanol was removed on a rotary evaporator. The product was washed three times with saturated aqueous sodium chloride and dried over sodium sulfate. Oil conversions were determined using the ^{1}H NMR technique described by Gelbard *et al.* [21] on a Varian Gemini-200 instrument operating at 200 MHz. As reported in [21], the methylene protons adjacent to the ester groups in the triglyceride and fatty acid methyl esters appear at 2.3 ppm and the methoxy protons of the methyl esters appear at 3.7 ppm. By integrating the areas (A) under the signals at 2.3 and 3.7 ppm and using the following equation, the yield of methyl esters was calculated:

$$\text{Methyl esters yield (\%)} = 100 \times \left(\frac{2 \times A_{3.7}}{3 \times A_{2.3}}\right)$$

Note that this yield is equivalent to the conversion of triglyceride to methyl esters (i.e., the product of triglyceride conversion and selectivity to methyl esters). Mono- and diglyceride yields are not determined by this method.

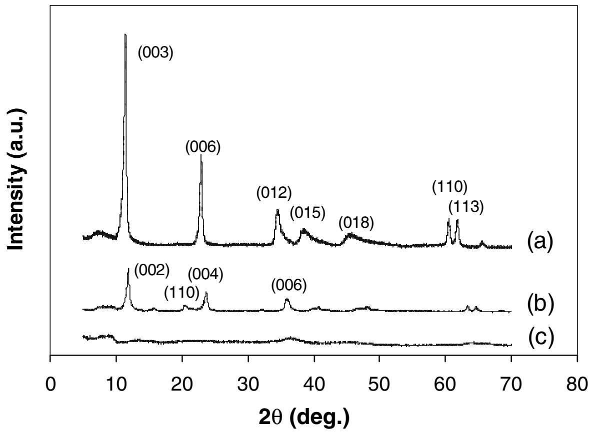

Figure 1. Powder X-ray diffractograms: (a) Mg–Al LDH, (b) Li–Al LDH, (c) Li–Al LDH after calcination at 450 °C.

3. Results and discussion

3.1. Catalyst characterization

The focus of this study was a Li–Al LDH catalyst, $[Al_2Li(OH)_6](CO_3)_{0.5} \cdot mH_2O$, prepared by co-precipitation. In addition, samples of a Mg–Al LDH and a Li-promoted γ-alumina were prepared for comparison purposes. Physical data for the catalysts are given in table 1. The Li–Al and Mg–Al LDH samples both exhibited X-ray diffractograms characteristic of hydrotalcite-type compounds [13, 22] (figure 1), while the diffractogram of the Li-promoted alumina (not shown) indicated the presence of γ-Al_2O_3 and $LiAlO_2$. For the Li–Al LDH, elemental analysis indicated a Li:Al stoichiometry of 1:4.3, as compared to the expected 1:2 stoichiometry. This suggests that either lithium incorporation in the gibbsite-type layers is incomplete, or that a separate, X-ray amorphous aluminum phase is present, such as pure gibbsite or boehmite. Upon calcination at 450 °C the LDHs decomposed via decarboxylation and dehydroxylation to form mixed oxides, with an accompanying increase in surface area. For the calcined $[Al_2Li(OH)_6](CO_3)_{0.5} \cdot mH_2O$, broad, weak diffraction lines observed at ca. $2\theta = 37°$ and $2\theta = 65°$ can be attributed to poorly crystalline γ-Al_2O_3.

The strength of the basic sites for each catalyst was assessed using a series of basic indicators. Methanol was used as the solvent so that the measured surface basicity would provide a reasonable reflection of that expected under reaction conditions. From these measurements the following order of basicity was determined (from strongest to weakest): calcined Li–Al mixed oxide ≈ calcined Mg–Al mixed oxide ≈ $LiOH/Al_2O_3$ > uncalcined Li–Al LDH. The basicity ranges are summarized in table 2. It should be appreciated that these measurements provide a measure of Brønsted basicity only, given that the H_ scale cannot be directly related to the strength of Lewis base sites.

Table 2
Measured basicity of calcined catalysts[a]

Catalyst	Base strength
Li–Al	$15 > H\_ > 10.1$
Li–Al (uncalcined)	$10.1 > H\_ > 9.3$
Mg–Al	$15 > H\_ > 10.1$
$LiOH/Al_2O_3$	$15 > H\_ > 10.1$

[a] Calcination conditions as for Table 1.

Table 1
Physical characteristics of prepared catalysts

Composition	LDH (as synthesized)			After calcination[a]	
	Surface area (m^2g^{-1})	Pore volume (cm^3g^{-1})	Crystallite size (Å)	Surface area (m^2g^{-1})	Pore volume (cm^3g^{-1})
Mg–Al	80	0.483	169	209	0.636
Li–Al	76	0.388	163	152	0.569
$LiOH/Al_2O_3$	–	–	–	91	0.393

[a] 450 °C/2 h for LDHs, 500 °C/3 h for $LiOH/Al_2O_3$.

3.2. *Comparison of calcined Li–Al and Mg–Al layered double hydroxide catalysts in soybean oil transesterification*

Transesterification experiments were performed at reflux temperature, initially using a fixed methanol to soybean oil mole ratio of 15:1 and a catalyst charge of 1wt% (based on the quantity of soybean oil used). The results are collected in table 3. The calcined Li–Al LDH exhibited considerably higher activity for the transesterification reaction than its calcined Mg–Al analogue, achieving a 53% yield of methyl esters after 1 h against a yield of $<3\%$ for the Mg–Al catalyst. Given the similar results of the Hammett indicator measurements for the two materials, these results suggest the involvement of Lewis basic sites in transesterification catalyzed by the calcined Li–Al LDH. In comparison, the Li-promoted γ-alumina showed low activity (6% methyl esters yield), despite possessing the same Li loading as the calcined Li–Al LDH. This is confirmation that the lithium species in the two catalysts are chemically very different with different basic strengths.

A homogeneous catalyst, NaOH, was likewise tested for comparison purposes. As expected it showed the highest yield of methyl esters (at a reaction time of only 0.5 h), although in comparison the Li–Al LDH catalyst nonetheless shows promising activity.

3.3. *Influence of calcination temperature*

As shown in table 4, the calcination temperature used has a significant impact on the activity of the Li–Al LDH catalyst in soybean oil transesterification. For the uncalcined form almost no methyl esters are formed, consistent with the weak basicity of the material. This contrasts with the high activity observed for the mixed oxide form, the optimum calcination temperature appearing to be around 400 °C. The exact nature of the active sites in calcined $[Al_2Li(OH)_6](CO_3)_{0.5}\cdot mH_2O$ is unclear, but they are most likely associated with highly dispersed Li_2O, present in a matrix of γ-Al_2O_3. As shown by thermogravimetric analysis (figure 2), decomposition of $[Al_2Li(OH)_6](CO_3)_{0.5}\cdot mH_2O$ commences at 130 °C and extends up to ca. 450 °C, with a DTG maximum at 204 °C. Initial weight loss is believed to correspond to elimination of the interlayer water [23], however, it is clear that this process overlaps with carbonate decomposition and the elimination of hydroxyl groups. According to published XRD data [24], the lamellar structure of $[Al_2Li(OH)_6](CO_3)_{0.5}\cdot mH_2O$ collapses when heated above 240 °C, although IR data from the same study suggest that CO_2 is eliminated in successive stages, with residual carbonate ions present at temperatures as high as 500 °C. Above this temperature, a slow phase transition to $LiAlO_2$ and $LiAl_5O_8$ occurs. From this it appears that a calcination temperature of 400–450 °C represents the optimum for decomposition of the LDH to the mixed oxide without formation of less basic (and lower surface area) $LiAlO_2$ and $LiAl_5O_8$ phases.

Table 3
Transesterification of soybean oil with methanol using different base catalysts[a]

Catalyst	Reaction time (h)	Yield of methyl esters (%)
NaOH	0.5	86
Mg–Al	1	<3[b]
Li–Al	1	53
$LiOH/Al_2O_3$	1	6

[a] Reaction conditions: 1wt% catalyst, MeOH:oil = 15:1, reflux temperature.
[b] 3wt% catalyst used. Catalysts calcined as for Table 1.

Table 4
Effect of Li–Al LDH calcination temperature on soybean oil transesterification[a]

Calcination temperature (°C)	Yield of methyl esters (%)
–	2
300	38
400	63
450	53
500	52
600	42

[a] Reaction conditions: 1 h reaction time, 1wt% catalyst, MeOH:oil = 15:1, reflux temperature.

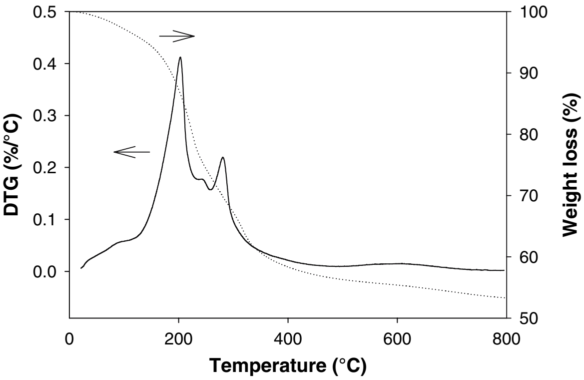

Figure 2. TG and DTG curves for $[Al_2Li(OH)_6](CO_3)_{0.5}\cdot mH_2O$.

3.4. *Influence of reaction conditions*

In order to determine the optimum reaction conditions, the influence of three parameters on soybean oil transesterification was examined: catalyst charge, reaction time and methanol to oil mole ratio. The results of experiments in which the first two of these parameters were varied are shown in figure 3. The catalyst charge was examined at three levels: 1, 2 and 3wt%, expressed as a weight percentage of the soybean oil used. In the absence of catalyst, no soybean oil conversion to methyl

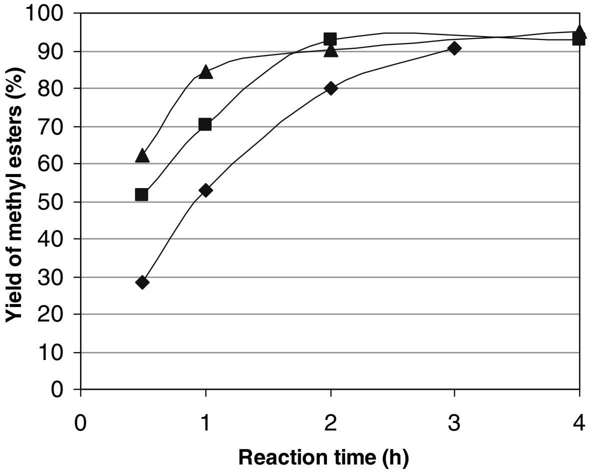

Figure 3. Effect of catalyst charge and reaction time on soybean oil transesterification with methanol: (◆) 1wt%, (■) 2wt%, () 3wt%. Catalyst calcined at 450 °C. MeOH:oil = 15:1, reflux temperature.

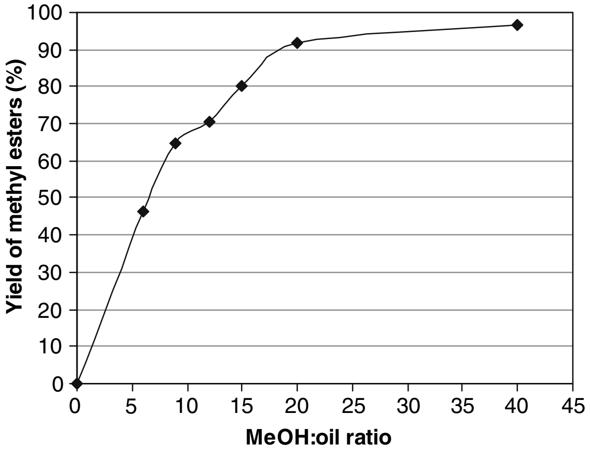

Figure 4. Effect of methanol:oil mole ratio on soybean oil transesterification with methanol. Catalyst calcined at 450 °C. Reaction conditions: 1wt% catalyst, 2 h reaction time, reflux temperature.

esters was observed. Increasing the catalyst charge resulted in a progressive increase in the yield of methyl esters at short reaction times (e.g., 0.5 h, 1 h). Similarly, increasing the reaction time for a given catalyst charge showed a positive effect on the conversion to methyl esters. For the catalyst charge of 2wt%, the maximum yield attainable (94 ± 2%) was achieved at a reaction time of 2 h.

Given that trigylceride transesterification consists of a sequence of three reversible reactions in which the triglyceride is successively transformed into diglyceride, monoglyceride and finally glycerol and fatty acid methyl esters, it follows that the mole ratio of methanol to soybean oil influences the conversion to methyl esters. Whereas the reaction stoichiometry requires three moles of methanol for each mole of triglyceride, in practice an excess of methanol is used to drive the reaction towards completion. The magnitude of this excess is reported to influence the transesterification rate, the optimum methanol to oil ratio being different for different catalysts [1]. As shown in figure 4, the conversion of soybean oil to methyl esters in the presence of the calcined Li–Al LDH catalyst exhibits a strong dependence on the methanol to oil ratio. Note that the yields of methyl esters shown in the figure do not correspond to equilibrium values. Thus, the methanol to oil ratio clearly influences the reaction rate, in addition to affecting equilibrium conversion levels. The maximum rate under these conditions (as reflected in the measured methyl ester yields), was obtained at a mole ratio of approximately 20:1, beyond which additional methanol had minimal effect.

3.5. Catalyst deactivation

In order to confirm the heterogeneous nature of the calcined Li–Al LDH catalyst, lithium solubility in the reaction mixture was examined for a run using 3wt% catalyst and a reaction time of 1 h. Assuming that all of the dissolved lithium was extracted into the aqueous NaCl solution used for washing the reaction product, the lithium concentration measured by ICP-OES indicated that 3.6% of the lithium present in the catalyst had been leached (analyses showed that the Li content of the NaCl was negligible). This suggests that the observed catalytic activity is largely heterogeneous in nature. To confirm this, additional experiments were performed. In the first of these, soybean oil transesterification was allowed to proceed to 51.6% completion, at which point the catalyst was isolated by hot filtration using a 0.5 μm filter. The filtrate was then heated at the reaction temperature for a further 1 h so that any residual catalyst in the filtrate would facilitate further conversion, and subsequently analyzed by ^{1}H NMR spectroscopy. A slight increase in the yield of methyl esters from 51.6% to 52.8% was noted. However, the typical standard deviation for identical transesterification runs with fresh catalyst (1wt% catalyst, 1 h reaction time) is 4.4%, such that the difference between 51.6% to 52.8% is considered to be insignificant. Hence, the dissolved lithium appears to possess little, if any, catalytic activity.

In addition, a series of recycling experiments was performed. For this purpose, an initial transesterification run was conducted using a catalyst charge of 3wt% and a reaction time of 1 h. The catalyst was then isolated by filtration, washed, dried and re-calcined. Given the difficulty of recovering all of the catalyst from the filter, the used catalyst was re-tested as a 2wt% charge and then subsequently recycled and tested again as a 1wt% charge. Other experimental variables were held constant. The results of these tests are summarized in figure 5, which for comparison purposes shows the results of runs performed with the same amounts of fresh catalyst. Error bars indicate the pooled standard deviation for experiments with 1 and 3wt% fresh

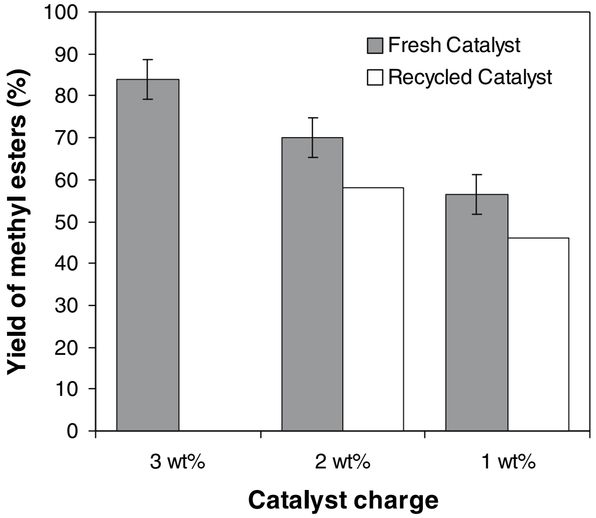

Figure 5. Results of transesterification experiments using fresh and recycled catalyst. Catalysts calcined at 450 °C. Reaction conditions: 1 h reaction time, MeOH:oil ratio = 15:1, reflux temperature. Error bars represent a pooled standard deviation for experiments done with 1 and 3wt% fresh catalyst.

catalyst. According to these results, after one recycle the catalyst appears to have decreased in activity, however, the yield of esters measured for the catalyst subjected to two recycles is only slightly lower than that obtained with fresh catalyst; in fact, the difference is on the same order of magnitude as the observed experimental variability. Overall it seems that there is some small degree of lithium leaching from the catalyst, and, hence, minor deactivation. Fixed bed experiments at much longer operating times will be required in order to determine whether lithium leaching is a serious issue for the long term stability of the catalyst.

4. Conclusions

Calcined $[Al_2Li(OH)_6](CO_3)_{0.5}\cdot mH_2O$ is an effective catalyst for the transesterification of soybean oil with methanol. The calcination temperature of the catalyst exerts a significant influence on its activity. A temperature of 400–450 °C was found to be optimal, corresponding to decomposition of the layered double hydroxide to the mixed oxide without formation of less basic (and lower surface area) $LiAlO_2$ and $LiAl_5O_8$ phases. At the reflux temperature of methanol, near quantitative conversion of the soybean oil was achieved at low catalyst loadings (2–3wt%) and short reaction times (~2 h). Catalyst recycling studies showed that the catalyst maintained a high level of activity over several cycles, although analyses indicate that a small amount of lithium is leached from the catalyst.

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