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LITHIUM CONTAINING MgAl MIXED OXIDES OBTAINED FROM SOL-GEL HYDROTALCITE FOR TRANSESTERIFICATION

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Abstract – The innumerous advantages of heterogeneous catalysts employed in biodiesel production have stimulated the search for a solid catalyst capable of replacing the industrially used homogeneous catalysts. This paper investigates the effect of the sol-gel method in the catalytic activity and stability of Li-MgAl mixed oxides prepared by the "*in situ*" lithium addition to a MgAl hydrotalcite. The analyses based on N_2 physisorption, thermogravimetric analysis, X-ray diffractometry, scanning electron microscopy and temperature-programmed desorption of CO_2 were carried out to elucidate the properties of the catalysts. Considerable differences in the physico-chemical properties of the catalysts were observed with the Li addition. Li reduced the surface area and increased the crystallite size of the oxides. Furthermore, Li-MgAl mixed oxides prepared by the calcination of the sol-gel MgAl hydrotalcites presented substantial morphological differences when compared to the same oxides obtained by heat treatment of hydrotalcites synthesized via the conventional co-precipitation route. Furthermore, Li increased the number and strength of the base sites which resulted in the increase of the oxide reactivities towards the transesterification reaction between methyl acetate and ethanol. The activity was dependent on the Li loading on the catalysts. The catalyst containing only 5 wt.% Li turned out to be highly active (≈ 85% conversion at 50°C, ethanol/methyl acetate molar ratio = 6/1, 4 wt.% of catalyst and 30 min of reaction). Stability tests showed that the Li-MgAl catalysts lose activity after 3 reuse cycles.

Keywords: hydrotalcite; sol-gel method; transesterification; lithium; mixed oxide; heterogeneous catalysis.

INTRODUCTION

In recent years there has been a growing awareness concerning the rational use of natural resources and the need to introduce pollution prevention practices, and development and use of clean technologies (Aransiola et al., 2014). As a result, extensive research has been performed in order to obtain alternatives to conventional fossil diesel fuels. One of the most attractive options is biodiesel since it is non-toxic, renewable and biodegradable. Biodiesel is usually produced from triglycerides (vegetable oils or animal fats) by a transesterification reaction with a short-chain alcohol (mainly methanol or ethanol). The reaction requires the presence of a catalyst, and homogeneous base catalysts (NaOH, KOH or its methoxides) have been industrially employed (Bart et al., 2010). However, the use of heterogeneous catalysts has been pointed out as the main significant improvement to the process. The solid catalyst can be easily separated from the final product and there is no need of water washing to remove the catalyst, which could reduce the biofuel production cost (Hanna and Isom, 2009).

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The innumerous advantages of the heterogeneous process have stimulated the search for a solid catalyst capable of replacing those used industrially for biodiesel production. In this context, MgAl mixed oxides derived from hydrotalcite compounds have been evaluated as solid base catalysts for transesterification and revealed to be promising for this application (Xie et al., 2006; Di Serio et al., 2012; Hájek et al., 2015). These ordinary MgAl mixed oxides have also been modified by incorporation of metal ions such as Na^+ and K^+ (Tittabut and Trakarnpruk, 2008), Fe^{3+} (Wang et al., 2012), Co^{2+}, Cu^{2+}, Cr^{3+} and Fe^{3+} (Veiga et al., 2013), and Zn^{2+}, Co^{2+}, Fe^{3+} and La^{3+} (Sun et al., 2014) in order to tailor the catalyst acid-base properties and consequently its performance for transesterification. Recent studies have also been dedicated to evaluate the effect of introducing non-metal species, such as fluorine (Lima et al., 2012), and also KF salt (Guzmán-Vargas et al., 2015), in the textural and basic properties and/or catalytic activity for transesterification of mixed oxides obtained from hydrotalcite-like compounds. For KF-modified CaAl hydrotalcites, Chen et al. (2014) investigated the influence of the impregnation solvent on the catalytic activity. They found that the catalysts synthesized in methanol displayed excellent activity for transesterification.

An inspection of published papers focused on metal-based MgAl mixed oxides shows that most authors adopt a similar procedure for synthesis of such catalysts, in which the MgAl oxides are obtained by the thermal treatment of MgAl hydrotalcite synthesized by a co-precipitation route. Therefore, this project was undertaken to evaluate the effect of the sol-gel method in the synthesis of MgAl hydrotalcite and the catalytic activity and stability of the obtained MgAl mixed oxides modified by Li for transesterification. The sol-gel method enables a high degree of control over the catalyst preparation, which allows the catalyst properties to be "molded" by varying the process parameters such as pH, reaction time and temperature, type of solvent and metal precursor used. Furthermore, the synthesis of catalysts by the sol-gel method allows the direct addition of the metal precursor *in situ* during the process. To the extent of our knowledge, there is no other paper in the literature that describes the synthesis of MgAl mixed oxides modified by Li obtained from sol-gel hydrotalcites.

MATERIALS AND METHODS

Synthesis of the catalysts

A sol-gel method based on Prinetto et al. (2000) was used to synthesize hydrotalcite (HT) compounds with a Mg/Al molar ratio of 4. Briefly, 0.15 mol of $Mg(NO_3)_2.6H_2O$ (Sigma-Aldrick) was dissolved in 120 mL of ethanol (Synth, 99.5% v/v) containing 3.2 mL of HCl (Baker, 35% v/v). Another solution containing 0.038 mol of $Al(NO_3)_3.9H_2O$ (Synth) dissolved in 80 mL of ethanol was added under constant stirring. The final pH of the mixture was adjusted to 10 by the dropwise addition of NH_4OH (Mallinckrodt Chemicals, 30% v/v). The resulting mixture was then constantly stirred until the gel formation (24 h). The obtained gel was repeatedly washed with distilled water and oven dried at 80°C for 24 h.

The Li-based catalysts were prepared by using a similar method described for MgAl hydrotalcite synthesis. However, the precursor of the Li^+ was added *in situ*. For that, $LiNO_3$ (Acros Organics, 99+%) was dissolved in 60 mL of ethanol and added to the mixture just before the pH adjusting. After 24 h of stirring, the obtained gel was oven dried at 80°C for 24h. The catalysts were prepared at the lithium loadings of 3, 5, 10 and 15 wt.% [$Li^+/(Li^+ +$ mixed oxide)]. It must be mentioned that the mixed oxide weight was established by TGA analyses at the desired calcination temperature. The MgAl and Li-MgAl mixed oxides were prepared by the calcination of the HT MgAl and Li^+ containing HTs, respectively. The thermal treatment was performed under air atmosphere in an EDG oven (3P-S 1800) at a heating rate of 5°C min^{-1} from room temperature up to 600°C and kept for 2 h at this temperature. The catalysts were named MgAl and x Li-MgAl, where 'x' is the lithium loading expressed in wt.%.

Characterization of the materials

The materials were characterized by powder X-ray diffractometry in a Rigaku Multiflex using Cu Kα radiation (λ=1.5406 Å) in the range 2θ from 5° to 80°, with a scan rate of 2° min^{-1} and a step width of 0.02°. The crystalline phases were identified using the Powder Diffraction File (PDF) database of the Joint Committee on Powder Diffraction Standards (JCPDS). The oxides crystallite sizes were calculated by the Scherrer equation using the main diffraction peak ($2\ \theta \approx 43°$) from the (200) MgO plane. Thermogravimetric analyses were carried out using a Shimadzu DTG-60H equipment (simultaneous DTA-TG apparatus). The samples were heated at a rate of 10°C min^{-1} from room temperature to 1000°C under an air flow of 50 mL min^{-1}. Surface areas (BET method), pore volumes (BJH method applied to desorption isotherms) and the pore size distributions of the calcined samples were determined by N_2 physisorption at 77K in a Quantachrome NOVA 1200. The morphology of the catalysts was characterized by scanning electron microscopy (SEM) on a FEI Magellan 400 L microscope. A Varian SpectrAA-200 atomic emission spectrometer was used to measure the lithium concentration in the catalysts (after calcination). For that, duplicate samples were digested with a mixture of HCl (Quimis, 37% v/v) and HNO_3 (Synth, 65% v/v), and H_2O_2 (Synth, 29% v/v) was used as an auxiliary oxidizing agent.

The basic properties of the catalysts were determined by temperature programmed desorption of CO_2 (TPD of

CO_2) in an AutoChem II chemisorption analyzer equipped with thermal conductivity detector (TCD). The samples (100 mg) were pretreated under He flow (50 mL min^{-1}) until the corresponding calcination temperature (T=600°C) with a heating rate of 20°C min^{-1} and then cooled to 100°C. The CO_2 adsorption was performed at 100°C for 1 h using a CO_2 flow of 50 mL min^{-1}. This was followed by helium purge (flow of 30 mL min^{-1}, temperature of 100°C for 1 h) to remove weakly adsorbed CO_2. The samples were cooled to 50°C and the CO_2 desorption profiles were obtained by heating the samples from 50 to 600°C, under He (30 mL min^{-1}) using a heating rate of 10°C min^{-1}.

Catalytic tests

The catalytic activity was evaluated in the transesterification model reaction between methyl acetate (Vetec, 99% v/v) and ethanol (Synth, 99.5% v/v). Compared to the transesterification reaction of vegetable oils, the model reaction is easier to perform and the formed products (methanol and ethyl acetate) are quickly monitored by gas chromatography (run time ≈ 4.3 min). It is worth mentioning that ethanol was selected as the alcohol source due to its renewable origin.

The experiments were carried out under optimized conditions with detailed description elsewhere (Castro et al., 2011; Castro et al., 2014). In short, the catalytic tests were performed in triplicate in small batch reactors with magnetic stirring, using an ethanol/methyl acetate mol ratio of 6/1, catalyst loading of 4 wt.% (wt. catalyst/wt. of the reaction mixture), temperature of 50°C and 30 min of reaction. The reaction products were analyzed in a Shimadzu gas chromatograph (GC 2010) equipped with flame ionization detector (FID) and Rtx®-1 capillary column (30.0 m x 0.32 mm i.d. x 3.00 μm film thicknesses). Column, injector and detector temperatures were held, respectively, at 65°C, 150°C and 170°C. Helium was used as carrier gas at a linear velocity of 40.0 cm.s^{-1} and 1.0 μL samples were injected manually in the split mode (ratio 1:150).

The catalytic activity was also expressed in terms of the turnover frequency (TOF), calculated as the number of moles of methyl acetate converted per active basic site per second of reaction. It is important to mention that the TOF was calculated considering only the strong basic sites detected by TPD of CO_2, since the weak basic sites of the Mg(Al)O catalyst were not active for transesterification reaction under the studied conditions (see Table 2).

Stability tests

The reuse of the catalysts in different batches was investigated. After reaction, the solid catalyst was separated from the reaction mixture by centrifugation. The supernatant solution was carefully removed and analyzed by GC. A new reaction mixture was then placed to react with the used catalyst. This process was repeated for subsequent reuse cycles and all reactions were performed under the same conditions described for catalytic evaluation. The reuse assays were also performed in triplicate. It should be highlighted that the basic catalysts were not washed nor dried in order to avoid their contact with atmospheric air, thereby preventing carbonation of the material.

In addition, chemical analysis of the reaction mixture was carried out in order to verify the occurrence of Li leaching from the catalyst to the solution. For that, the solution was filtered after the first reaction cycle by using syringe filters (0.45 μm pore size), the volatile compounds were evaporated and the residual metals were resuspended with HNO_3 solution (1% v/v) for the chemical analysis in a Varian SpectrAA-200 Atomic Emission Spectrometer.

RESULTS AND DISCUSSION

Characterization of the catalysts

The structure of the catalysts was investigated by XRD. The XR diffractions of the sol-gel MgAl hydrotalcite are shown in Fig. 1-a and attest to the formation of the hydrotalcite lamellar structure [JCPDF 14-0191]. Figure 1-b presents the XRD of the MgAl mixed oxide and Li-MgAl. As expected, the heat treatment of the hydrotalcite generated a MgAl mixed oxide with periclase structure (MgO) [JCPDS 75-1525]. No AlO_x cristalline phases were detected, which suggests the formation of a solid solution between MgO and AlO_x during calcination. In fact, the ionic radii of Mg^{2+} (0.72 Å) and Al^{3+} (0.53 Å) are not so different (Lide, 1997; Barbosa et al., 2005) and the incorporation of Al^{3+} ions into MgO creates defects within the MgO lattice and causes structural promotion at high temperature during calcination (Di Cosimo et al., 1998).

In the case of the Li-MgAl oxides, the similar ionic radii of Li^+ (0.76 Å) and Mg^{2+} (0.72 Å) allows the Mg^{2+} substitution by Li^+ ions into the MgO lattice during calcination. The substitution of divalent by monovalent cations leads to the formation of O^{2-} anions of low coordination. These O^{2-} anions are located at the corners and edges of the MgO crystals and have high basic strength (Di Cosimo et al., 1998; Díez et al., 2006; Berger et al., 2007). In addition to that, some low intensity diffractions possibly indicate the presence of $LiAlO_2$, Li_2CO_3 and LiOH in the Li-MgAl oxides. The Li_2CO_3 and LiOH are probably formed from carbonatation and hydration of Li_2O, respectively. This can be the reason for the absence of diffractions related to the Li_2O compound. Li_2O was expected to be present in the Li-MgAl mixed oxides since this compound is generated during the thermal decomposition of $LiNO_3$ used in the synthesis procedure. The Li_2O can also be present in small particle size and/or highly dispersed over the oxide matrix. This finding is in agreement with Rynkowski et al.

(1996) and Díez et al. (2006), who reported the absence of diffractions for Li_2O for lithium promoted MgO. Furthermore, $LiNO_3$ diffractions (Fig. 1-b) were detected for the sample containing the highest Li loading (15 Li-MgAl), which reveals an incomplete decomposition of the lithium nitrate precursor during the calcination performed at 600°C. However, the temperature of 600ºC has been chosen as the calcination temperature of the catalysts in order to compare the properties and catalytic performance of the sol-gel Li-MgAl with the coprecipitated samples reported in our previous paper (Castro et al., 2011).

The thermal stability of the MgAl hydrotalcite under air atmosphere was investigated by thermogravimetric analyses (Fig 2). The TG/DTG (derivate weight loss) (Fig. 2-a) and DTA/DTG (Fig. 2-b) profiles showed representative transformations of hydrotalcite compounds (Lopez et al., 1997; Xie et al., 2006; Serrano-Lotina et al., 2011).

In Fig. 2-a and b, the first endothermic peak (centered at ≈ 137°C, with weight loss of ≈12%) can be associated with the elimination of the surface water along with the water present in the interlayer space. The weight loss of about 34% that occurred in the temperature range of 250 - 550°C can be related to the layer dehydroxylation and release of the anions (-OH) present in the interlayer space. These processes lead to the collapse of the hydrotalcite structure and the formation of the MgAl mixed oxide (Xie et al., 2006; Ramos-Ramírez et al., 2009). At temperatures above 550°C, the residual mass is almost constant, with a total weight loss of 48%.

Fig. 3-a and b compares the TGA profiles obtained for sol-gel hydrotalcite (before calcination) containing 5 and 15% of Li, respectively. It can be noted that the hydrotalcite containing only 5% Li (Fig. 3-a) is completely decomposed at a temperature near 580ºC. On the other hand, for the hydrotalcite containing 15% Li (Fig. 3-b), the complete decomposition occurs at about 650ºC. This finding attests that the Li addition into hydrotalcite induces changes in the thermal stability of the materials. The increased amount of $LiNO_3$ on the catalysts displaces the decomposition temperature toward higher values. The total weight loss (≈ 80% at 1000ºC, Fig. 3-a and b) is similar for both materials. This high weight loss observed for the Li containing hydrotalcites occurs because these samples were not washed during the synthesis procedure and all the aluminum, magnesium and lithium nitrates are eliminated during the heat treatment. Therefore, the TGA results indicate that 15 Li-MgAl is not completely decomposed during calcination performed at 600ºC and the residual $LiNO_3$ remains on the catalyst, thus corroborating the results obtained by XRD. However, it is already known that the residual $LiNO_3$ is not active for transesterification (Castro et al., 2011).

The effect of the Li addition on the catalyst morphology was investigated by SEM. The MgAl (Fig. 4-a) presents typical "platelet" morphology of the mixed oxides derived from hydrotalcite (Reichle et al., 1986; Xie et al., 2006; Tittabut and Trakarnpruk, 2008). However, the Li addition significantly affected the morphology of the oxides. The 5 Li-MgAl (Fig. 4-b) presents aggregates of round particles and a completely different morphology can be observed for 10 and 15 Li-MgAl. Fused and sintered particles with long format resembling needles along with plate forms of smooth surface can be seen for 10 Li-MgAl (Fig. 4-c). For15 Li-MgAl (Fig. 4-d), only needle forms can be observed. It must be mentioned that the sol-gel Li-MgAl morphology is rather different from the morphology of the co-precipitated Li-MgAl oxides that present large aggregates composed of round particles (Castro et al., 2011; Castro et al., 2013).

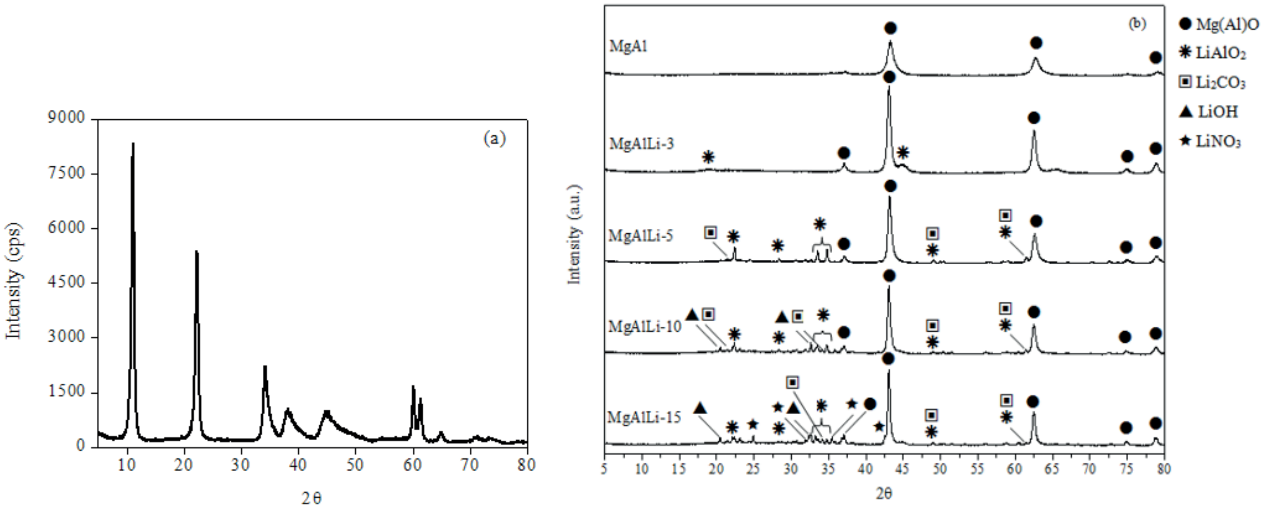

Figure 1. XRD of the sol-gel MgAl hydrotalcite (a) and MgAl and Li-MgAl mixed oxides (b).

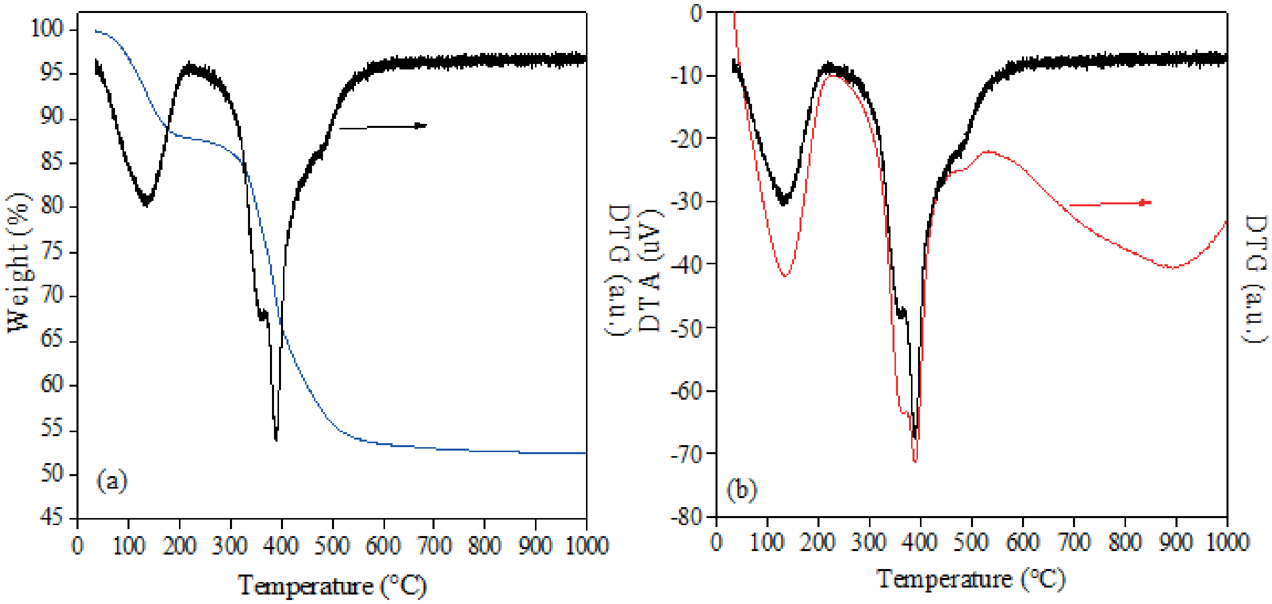

Figure 2. Thermal analysis TG/DTG (a) and DTA/DTG (b) of the sol-gel MgAl hydrotalcite.

The N_2 adsorption/desorption isotherms at 77 K for the MgAl and Li-MgAl oxides are shown in Fig. 5-a and 5-b, respectively. All materials presented similar isotherm shapes, classified as type IV, with an H3 hysteresis loop (it was not possible to obtain the isotherms for 15 Li-MgAl due to its very small N_2 adsorbed amount). Such isotherms are typical of mesopore-containing solids (2-50 nm) (Sing et al., 1985). The presence of mesopores in the catalyst is very important when this catalyst is applied for transesterification of triglycerides. The large pores assist the reactant diffusion into the solid to reach the active sites.

Table 1 provides the catalyst characterization such as crystallite size, BET surface area, pore volume and lithium loading in the oxides.

It is apparent from Table 1 that the crystallite size of the catalysts increases as the Li content increases. According to Rynkowski et al. (1996) and Berger et al. (2007), the thermal stability of MgO is strongly reduced in the presence of Li, which causes oxide sintering at elevated temperatures. As the MgAl mixed oxide presents the similar cubic structure of MgO, it is possible to infer that the Li addition to MgAl produces a similar sintering effect to that of the Li addition to MgO. In consequence of

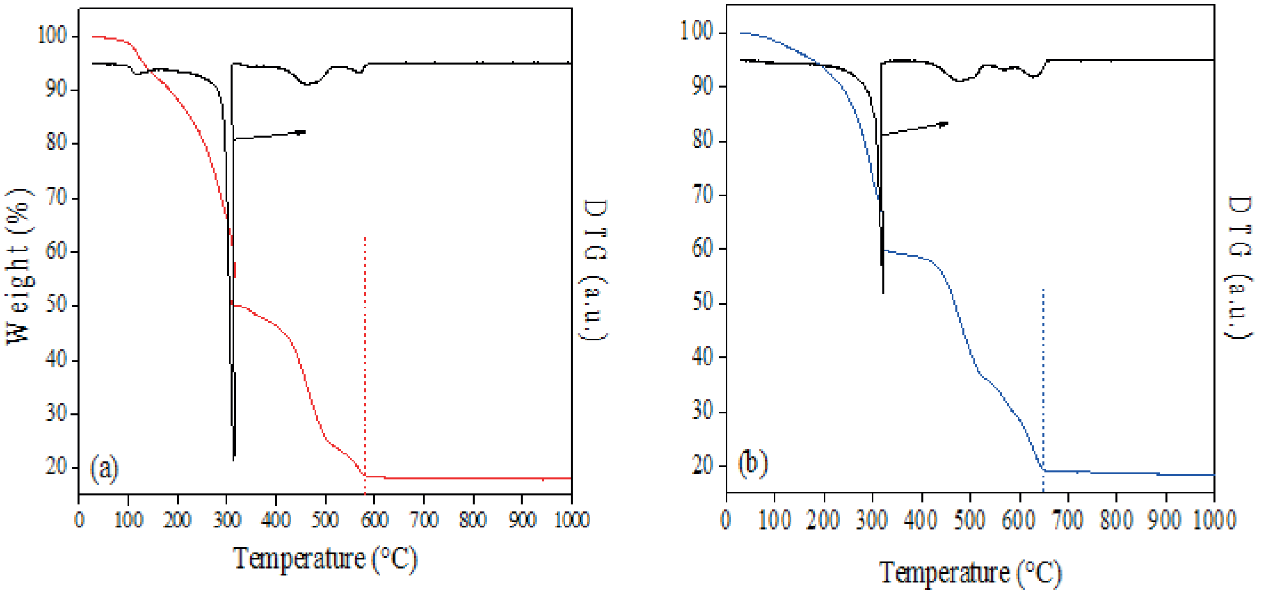

Figure 3. TG/DTG curves for the sol-gel MgAl hydrotalcite (before calcination) containing 5 wt.% of Li (a) and 15 wt.% of Li (b).

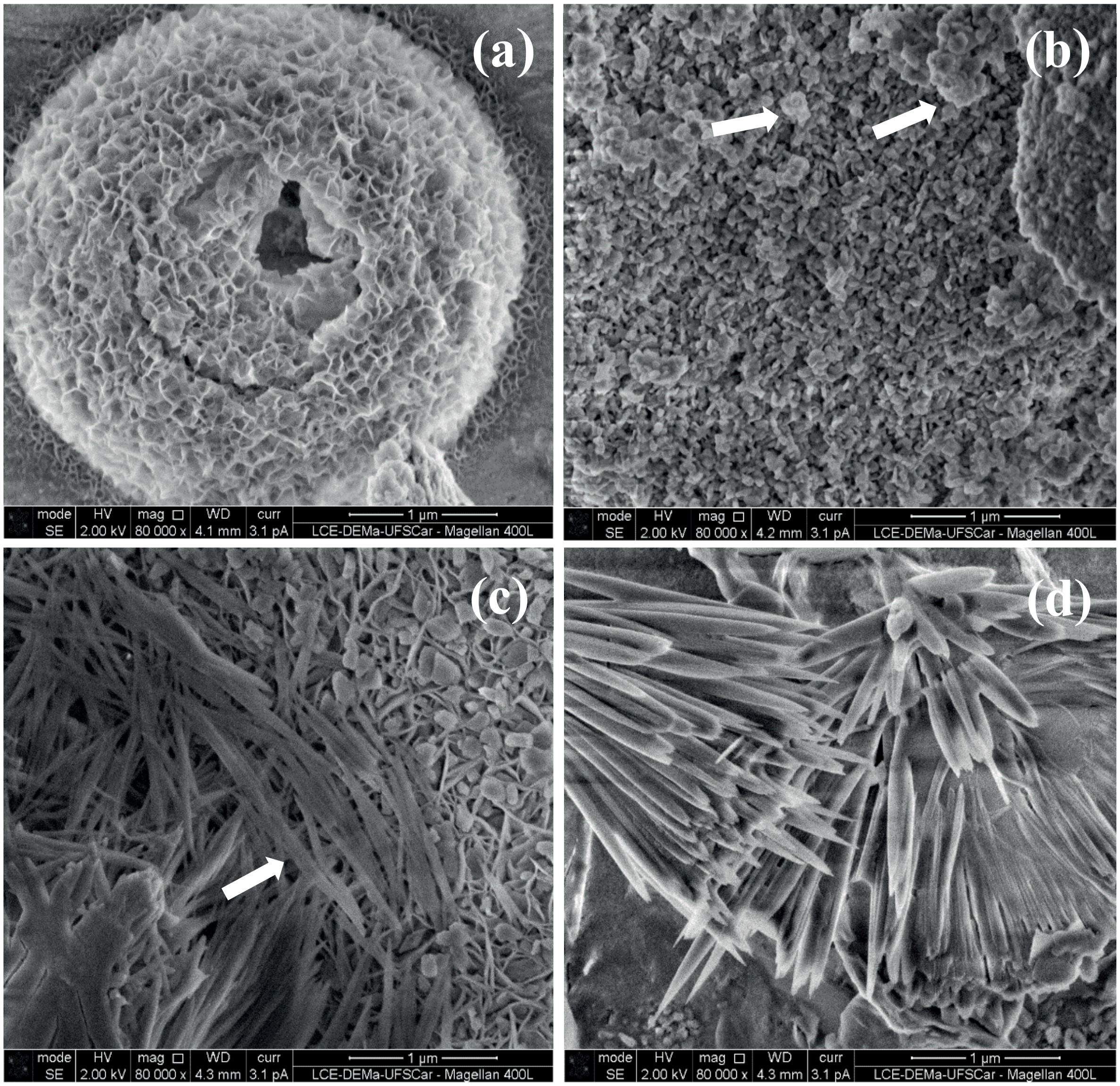

Figure 4. SEM micrographies of the MgAl mixed oxide (a), 5 Li-MgAl (b), 10 Li-MgAl (c) and 15 Li-MgAl (d).

the oxides sintering, an expressive reduction of the surface area and pore volume occurred with the Li addition into the MgAl mixed oxide. For example, the surface area of the MgAl is 155 $m^2 g^{-1}$ and it reduces to < 2 $m^2 g^{-1}$ for the 15 Li-MgAl (Table 1). This effect has also been reported for the Li-MgAl oxides obtained by the co-precipitation route. It was observed that the surface area was reduced from 201 $m^2 g^{-1}$ (MgAl) to 5 $m^2 g^{-1}$ for the sample containing 10 wt.% Li (Castro et al., 2011).

The reduction of the catalyst surface areas with the Li addition into the oxides is not desired since the catalytic process is a surface phenomenon and, in theory, the higher the surface area, the higher the reactivity. However, the activity is also dependent on the presence of the active sites on the surface, more precisely, the density of active sites on the surface, expressed in µmol m^{-2}. Therefore, it is also important to investigate the presence of basic active sites on the surface of the Li-MgAl mixed oxides and this characterization was performed by TPD of CO_2.

Figure 6 presents the TPD of CO_2 characterization performed for MgAl, 3-Li MgAl and 5-Li MgAl. In the next section it will be shown that the catalytic activity for 5, 10 and 15-Li MgAl is very similar. Thus, the basicity studies were performed only for the sample 5 Li-MgAl and the samples that presented no activity (3 Li-MgAl and MgAl) for comparison.

The TPD of CO_2 profile of the MgAl mixed oxide presented a low intensity desorption band at low temperature (≈170°C), thus revealing that this oxide is mainly composed of weak basic sites related to surface

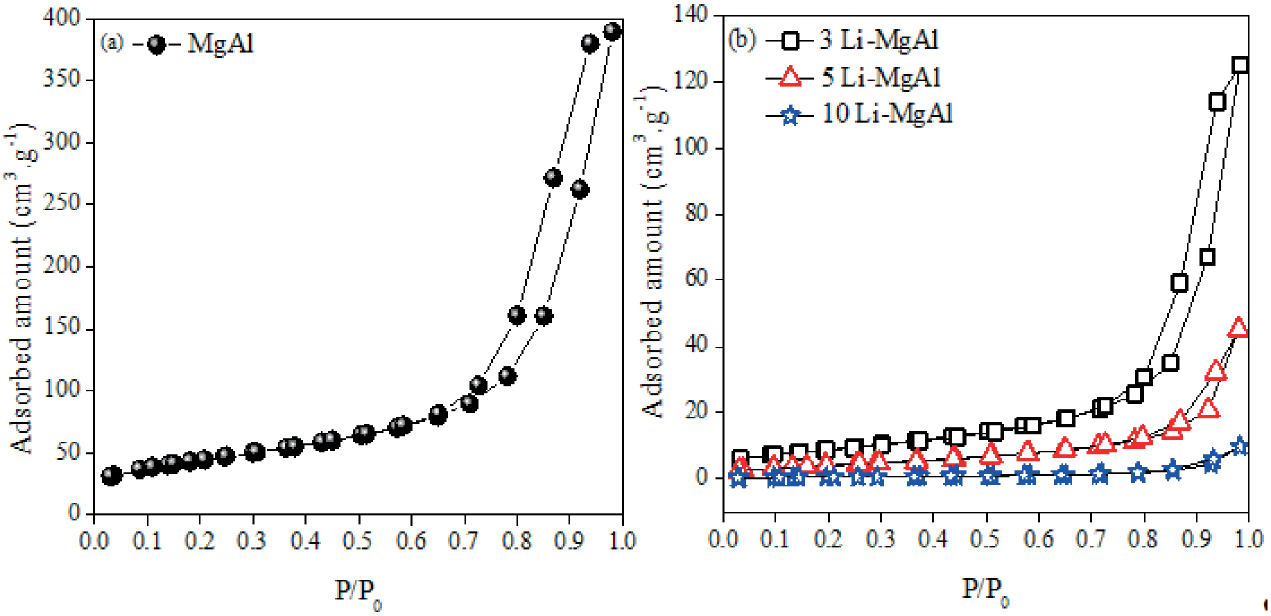

Figure 5. N_2 adsorption/desorption isotherms at 77 K of the materials.

hydroxyl groups (Wang et al., 2012). By adding 3% of Li into MgAl, a broad desorption band centered at about 270°C is observed. This indicates that Li increased the density of the basic sites on the catalyst surface (observed by the area under the TPD curve) and increased the strength of the basic sites (verified by the CO_2 desorption temperature; the higher the desorption temperature, the higher the basic strength). The medium strength basic sites are mainly associated with Mg^{2+}-O^{2-} and Al^{3+}-O^{2-} pairs (Díez et al., 2000) and possibly with Li^{+}-O^{2-} pairs. These sites are present mainly on 3 Li-MgAl. In the case of 5 Li-MgAl, besides the peak centered at 170°C, a large amount of strong base sites (centered at 400°C) can be clearly observed. The strong basic sites are probably attributed to isolated O^{2-} anions, of low coordination number, which are highly reactive (Díez et al., 2000; Díez et al., 2006).

The total basic site densities (n_b) of the studied catalysts were measured by integration of CO_2 TPD bands (Table 2). The TPD plots were deconvoluted into three desorption peaks with maximum desorption temperatures in the range of 160-190°C (weak base sites), 210-280°C (medium strength base sites) and 350-450°C (strong base sites). These results indicate that total n_b has a maximum value for 5 Li-MgAl and decreases with the reduction of the Li loading on the materials. The 5 Li-MgAl oxide also showed the highest amount of strong base sites. It must be highlighted that the strong basic site density on sol-gel 5 Li-MgAl (7.65 μmol m^{-2}) is even higher than that present on the 10 Li-MgAl catalyst prepared by co-precipitation (3.90 μmol m^{-2}) (Castro et al., 2013).

Catalytic evaluation

The catalyst performances for the model transesterification are presented in Fig. 7. The symbols represent the average conversion values and the standard deviations are indicated by bars.

It is possible to observe that the MgAl mixed oxide and the sample containing the lowest Li loading (3 Li-MgAl) presented no activity. In contrast,

Table 1. Crystallite size, BET surface area and lithium loading in the catalysts.

Catalysts	Crystallite size^a (nm)	Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Li^+ loading (wt. %)**
MgAl	13.2	155	0.610	-
3 Li-MgAl	18.7	62	0.200	3.2±0.10
5 Li-MgAl	18.9	16	0.072	4.2±0.07
10 Li-MgAl	22.6	2	0.016	6.5±0.28
15 Li-MgAl	27.8	<2*	<0.016	7.7±0.35

^{a}Obtained from XRD and Sherrer's Equation using the main diffraction peak of MgAl at 2θ = 43.0°.
* The surface area of the 15 Li-MgAl was not determined since it was too small (< 2 m^2 g^{-1}).
** Determined by Atomic Emission Spectrometer.

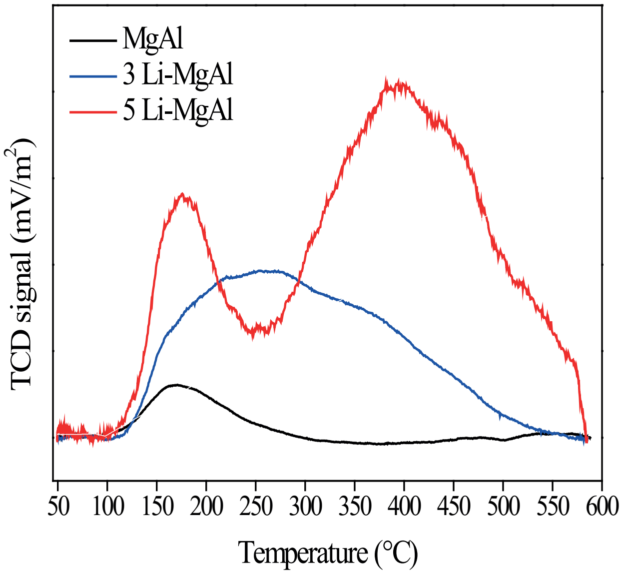

Figure 6. Temperature-programmed desorption profiles of CO_2 of the sol-gel MgAl and Li-MgAl mixed oxides.

Table 2. Basic site density for MgAl and Li-MgAl mixed oxides.

Catalysts	Density of base sites – n_b (μmol m^{-2})			
	Total n_b	Weak n_b	Medium n_b	Strong n_b
MgAl	0.54	0.42	0.13	0.00
3 Li-MgAl	4.23	0.22	1.79	2.22
5 Li-MgAl	9.16	1.34	0.17	7.65

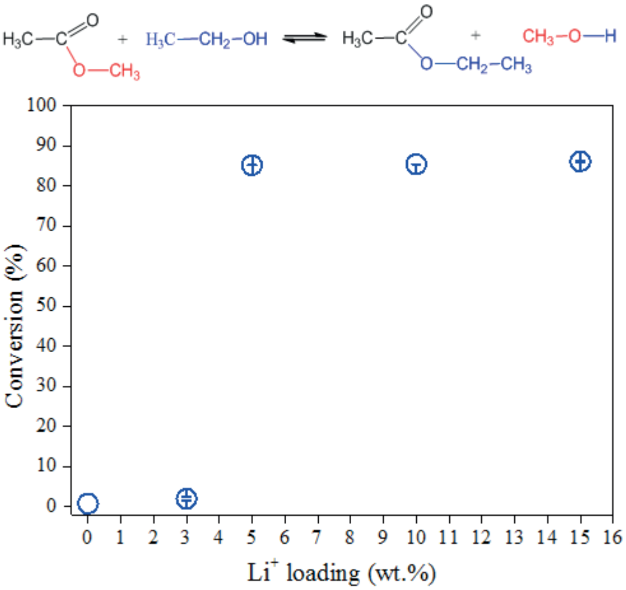

Figure 7. Transesterification reaction in the presence of the sol-gel MgAl mixed oxide and Li containing MgAl oxides.

the oxides with higher Li loadings (5, 10 and 15 Li-MgAl) exhibited high conversions, irrespective of the Li content. The catalytic results revealed that the activity for transesterification is strictly dependent on the presence of Li in the mixed oxides, since the catalyst without Li (MgAl) presented no activity. In addition, the activity is dependent on the Li loading on the catalysts.

This finding further supports the idea that Li is crucial in the creation of the active sites for transesterification. Although the surface area reduction occurred with the Li addition to the catalysts, the density of basic sites (μmol m^{-2}) markedly increased and this resulted in the enhanced catalytic performance for transesterification.

The TPD of CO_2 characterization revealed that the Li addition to the catalysts increased the total density of basic sites and, which seems to be more important, the density of strong basic sites. This can explain the sharp conversion increase observed when the Li loading on the catalyst increased from 3 to 5 wt.% (Fig. 7). The 3 Li-MgAl presents mainly basic sites of medium strength, leading to negligible conversion. On the other hand, 5 Li-MgAl presents a lot of strong basic sites, which resulted in high activity. Table 3 presents the turnover frequencies for the catalysts, which were calculated based on the strong basic sites. Considering the fact that the MgAl catalyst does not present basic sites of high strength (Table 2), the TOF value for this catalyst was not calculated. As shown in Table 3, a value 45-fold greater was obtained for 5 Li-MgAl compared to the TOF value for 3 Li-MgAl, and these values are within the expected range for most reactions involving heterogeneous catalysis (i.e., from 10^{-2} to 10^2 s^{-1}) (Thomas and Thomas, 1996).

Therefore, the results suggest that the strong basic sites, mainly associated with isolated O^{2-} anions are possibly the active sites for transesterification in the case of Li-MgAl mixed oxides. These isolated O^{2-} of low coordination are related to surface defects formed during the Mg^{2+} substitution by Li^+ due to their ionic radii similarity.

The great performance of the Li based MgAl oxides prepared by the co-precipitation route has already been reported in our previous papers (Castro et al., 2011; Castro et al., 2013). However, in the case of Li-MgAl oxides prepared by the sol-gel method, the Li loading required for activity is quite low, reaching about 85% of conversion with the catalyst containing only 5 wt.% Li. For co-precipitated samples, the Li loading required to achieve the same conversion was 10 wt.% Li (Castro et al., 2011).

Table 3. Turnover frequency (TOF) for model transesterification in the presence of the MgAl and Li-MgAl catalysts.

Catalysts	**TOF x10^3 (s^{-1})**
MgAl	-
3 Li-MgAl	5.9
5 Li-MgAl	275.0

This indicates that the Li interaction with HT prepared by the sol-gel route is different from that of the coprecipitated HT followed by Li impregnation. This is also evidenced by the changes caused in the morphology of the sol-gel and coprecipitated oxides. The *in situ* Li addition during the sol-gel HT synthesis increased the number of defects in the lattice of MgAl mixed oxide after calcination due to the closer Li interaction with the HT matrix when compared to the Li impregnation on the surface of co-precipitated HT.

Stability studies

The stability of the sol-gel Li-MgAl catalysts was investigated through its recycling and reuse during consecutive batch runs. The experiments were performed with the active catalysts for transesterification and the results are presented in Fig. 8. Vertical bars in each column represent one stardard deviation.

It can be clearly observed that, irrespective of the Li content, the catalysts lost their activity during recycling (Fig. 8-a). The conversion was reduced severely in the third reaction cycle. In an attempt to increase the catalyst stability, a representative sample of 15 Li-MgAl was calcined at a higher temperature of 700°C. The reuse experiments are shown in Fig. 8-b. Although the conversion increased slightly in the second and third runs, an apparent deactivation still occurs. It seems that, even though the Li interaction with the sol-gel MgAl oxide were different from the co-precipitated catalysts, a similar deactivation profile was observed, possibly due to the leaching phenomenon. Chemical analysis results for the 10 Li-MgAl sample revealed that lithium leaching to solution occurs, since approximately 500 mg L^{-1} of Li^+ was detected in the reaction mixture after the first reaction cycle.

CONCLUSIONS

The use of the sol-gel method for the synthesis of the Li-MgAl mixed oxides led to the formation of highly active catalysts for the model transesterification reaction. These materials were as active as the same oxides prepared by co-precipitation. However, the lithium loading required to reach the same conversion was 2-fold lower in the case of sol-gel samples. This result indicates that the Li interaction with the MgAl matrix is different when using the sol-gel route. This finding is supported by the morphological differences between the sol-gel (needle-like particles) and coprecipitated (round aggregates) samples. The catalyst performances for transesterification are closely related with the basicity of the catalysts. The conversion were dependent on the Li loading on the catalysts and related to the density of the strong basic sites on the catalysts. The strong basic sites in Li-MgAl are possibly related to O^{2-} anions of low coordination that are probably the active sites for reaction. The results of this study suggest that the very active sol-gel Li-MgAl catalysts are promising candidates to replace the homogeneous catalysts industrially used for transesterification. Nevertheless, the stability tests revealed that the catalysts reduce their activity during recycling. Further research should be carried out in order to investigate possible modifications in the synthesis procedure in an attempt to increase the Li-MgAl mixed oxides stability.

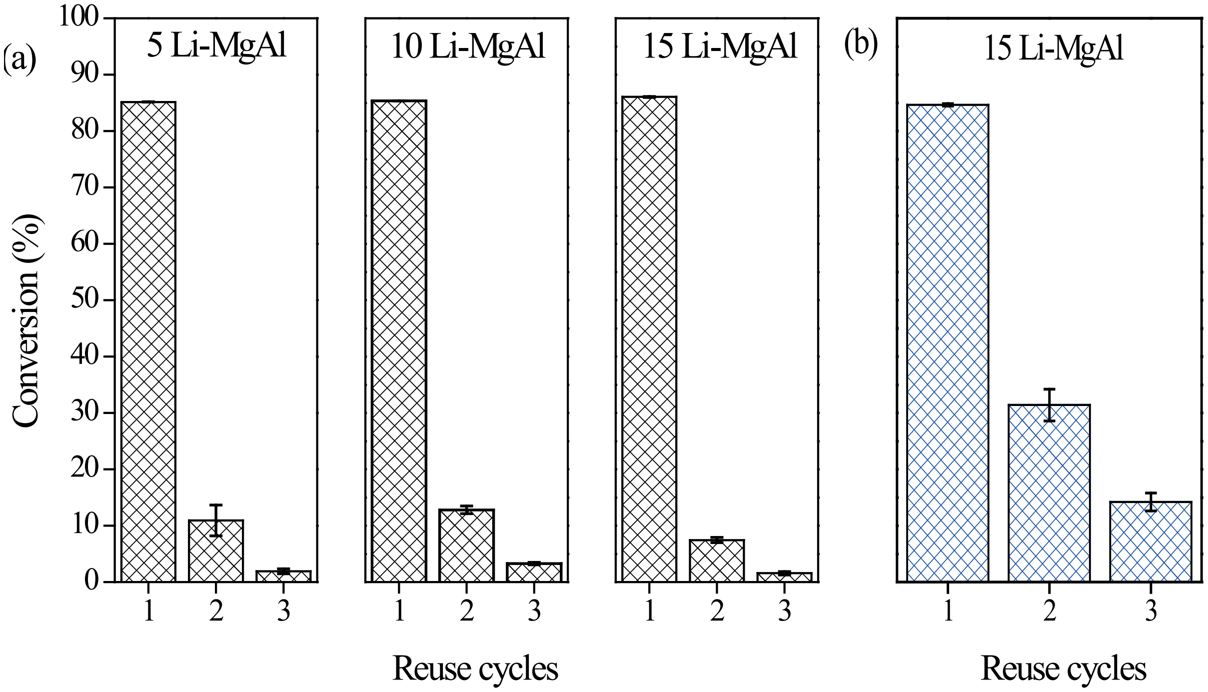

Figure 8. Reuse cycles for the transesterification reaction in the presence of the Li-MgAl oxides calcinated at 600°C (a) and 700°C (b).

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