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Support influence on the basicity promotion of lithium-based mixed oxides for transesterification reaction

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HIGHLIGHTS

► Lithium containing oxides for catalytic transesterification.
► The support nature strongly affect the basicity promotion of the Li containing oxides.
► The Li addition onto the catalysts increases the base site number and strength.
► Li/MgO and Li/Mg(Al)O exhibited high activity under mild reaction conditions (313 K).
► The reaction occurs through heterogeneous/homogeneous mechanism.

ARTICLE INFO

ABSTRACT

Solid catalysts comprising Li-based oxides were prepared by $LiNO_3$ impregnation onto supports with different acid/base properties (SiO_2, MgO, Al_2O_3 and Mg(Al)O mixed oxide obtained from hydrotalcite). The materials were characterized by means of XRD, N_2 physisorption, ICP–OES, FEG-SEM and TPD of CO_2. The oxide reactivities were evaluated using the model transesterification reaction between methyl acetate and ethanol under mild reaction conditions (313 K, ethanol/methyl acetate molar ratio = 6/1 and 0.2 wt.% of catalyst). Lithium impregnation onto silica and γ-alumina yielded inactive catalysts for transesterification. On the other hand, the lithium addition onto MgO produced an active catalyst and remarkably high conversions were obtained for Li/Mg(Al)O. The different supports used considerably affected the base site densities and base strengths of the Li-based catalysts. The base properties thus influenced the catalytic performance of the materials. Stability tests revealed the lithium leaching occurrence which resulted in some homogeneous contribution.

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1. Introduction

Transesterification of alkyl esters plays an important function in numerous applications such as biodiesel production. Biodiesel is a promising substitute to fossil diesel fuel because its renewable nature is effective in reducing greenhouse gas emissions. Commercially, biodiesel is produced by transesterification of triglycerides obtained from edible vegetable oils and animal fats with short chain alcohols to produce alkyl esters and glycerol [1]. Transesterification can be accomplished by an acid or base catalyst [1]. A great deal of interest has recently been stimulated by the use of heterogeneous catalysis in place of the homogeneous catalysis industrially employed for biodiesel production [2–4]. The use of solid catalyst has been pointed out as an option for simplifying the biodiesel process, reducing the production cost. The solid catalyst does not corrode the reactor, can be recycled, and is easily separated from biodiesel, generating an uncontaminated product [5].

Currently, a number of heterogeneous acid and basic catalysts have been developed and applied for biodiesel production, the basic compounds reported to exhibit the highest activity. They include calcium oxide [6], MgAl oxides derived from hydrotalcite [7–9], $MgO–La_2O_3$ and $CaO–La_2O_3$ [10,11], Li promoted CaO [12,13], etc. Although intensive investigations have been carried out, the synthesis of an active solid and recyclable catalyst is still a challenge.

In particular, lithium-based catalysts have shown to present a distinctive behavior compared to other alkali (Na, K and Cs) or alkaline earth (Ca, Sr and Ba) based catalysts [14,15]. Lithium incorporation onto MgO is reported to create strong basic sites [15]. In our previous paper, we have shown that MgAlLi mixed oxide is a very active catalyst for transesterification reaction under mild reaction conditions [16].

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Considering this, the motivation for the present investigation has been to elucidate how supports of different acid/base surface properties affect the formation of the active sites for transesterification promoted by lithium-based catalysts. Therefore, the supports chosen were a highly basic MgO, an amphoteric oxide γ-Al$_2$O$_3$ and a mixed oxide containing both Mg and Al obtained from hydrotalcite precursor. Furthermore, commercial SiO$_2$ has been selected as a reference support due to its large surface area and neutral surface properties.

2. Materials and methods

2.1. Synthesis procedure

The Mg–Al hydrotalcite was synthesized by the coprecipitation method at room temperature as described in [16]. Briefly, 100 mL of an aqueous solution containing 20.5 g of Mg(NO$_3$)$_2$·6H$_2$O and 7.5 g of Al(NO$_3$)$_3$·9H$_2$O with Al/(Al + Mg) = 0.2 was added dropwise into another solution containing 2.4 mol L^{-1} of (NH$_4$)$_2$CO$_3$ under vigorous stirring. The pH during the synthesis was held at 10 by the addition of NH$_4$OH (30% v/v). The precursors of the Al$_2$O$_3$ and MgO (boehmite Al(O)OH and brucite Mg(OH)$_2$, respectively) were prepared following the same procedure except that magnesium nitrate or aluminum nitrate were absent. The precipitates were aged at 338 K for 18 h and then washed with warm distilled water. The obtained solids were oven dried at 383 K for 24 h. These precursors were decomposed in air atmosphere using a heating rate of 10 K min^{-1} until 873 K and kept at this temperature for 0.5 h in order to obtain the corresponding oxides. Commercial Aerosil®380 was purchased from Degussa and used as silica source. For comparison, the Aerosil®380 was also "impregnated" with distilled water and calcined under the same conditions as the other support precursors.

The Li-based catalysts were prepared by the wet impregnation method. For that, LiNO$_3$ was dissolved into 20 mL of distilled water and placed in contact with an appropriated amount of the support precursor, i.e., boehmite – AlO(OH); brucite – Mg(OH)$_2$; MgAl hydrotalcite or Aerosil®380 – SiO$_2$. The amount of the support precursors AlO(OH) and Mg(OH)$_2$ were stoichiometrically calculated to generate the pure oxides: Al$_2$O$_3$ and MgO. The Aerosil®380 is already composed of pure oxide SiO$_2$. In the case of the Mg(Al)O oxide, the determination of the oxide weight formed by the hydrotalcite calcination was established by hydrotalcite TGA analysis (showed in [16]). Afterwards, the mixture (LiNO$_3$ aqueous solution + support precursor) was heated at 353 K under magnetic stirring until complete drying. The resulting powder was dried at 383 K overnight.

In our previous study [16], we found that the Li impregnation loading of 10 wt.% onto MgAl hydrotalcite produced the most active catalyst for transesterification reaction. Thus, nominal values of 10 wt.% Li were used for impregnation onto the different supports studied in this work. After LiNO$_3$ impregnation, the solids were calcined in a tubular furnace under air atmosphere at a heating rate of 10 K min^{-1} until 873 K and kept at this temperature for 0.5 h.

2.2. Supports and Li-based catalysts characterization

The lithium content in the catalysts was determined with an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP–OES, Varian-Vista). Nitrogen physisorption at 77 K was used for the BET surface area determination (Quantachrome, NOVA – 1200). The materials were also characterized by powder X-ray diffractometry (XRD) in a Rigaku Geigerflex spectrometer using Cu Kα radiation (λ = 1.5406 Å). The crystalline phases were identified using the Powder Diffraction File (PDF) database (JCPDS, International Centre for Diffraction Data). The catalyst morphology was studied by Field emission gun scanning electron microscopy (FEG-SEM) on a Philips XL-30 FEG microscope. The basic properties of the catalysts were investigated by temperature programmed desorption of CO$_2$ (TPD of CO$_2$). The samples were previously treated under N$_2$ flow heated at a rate of 10 K min^{-1} until 873 K and cooled to room temperature. The CO$_2$ adsorption was carried out at room temperature using a gaseous mixture of 3% of CO$_2$ in N$_2$ until surface saturation (5 min). Physically adsorbed CO$_2$ was removed by flushing with N$_2$ for about 1 h. Thus, the CO$_2$ desorption was performed by increasing the temperature at a rate of 10 K min^{-1} until 873 K and the flow containing the desorbed CO$_2$ passed through a methanation reactor. In this step, the desorbed CO$_2$ was converted into CH$_4$ on a Ni/Kieselghur catalyst at 673 K. Therefore, the CO$_2$ desorption was indirectly quantified by the produced CH$_4$ which was analyzed using a flame ionization detector (FID).

2.3. Catalytic tests

The catalytic activity was evaluated in the transesterification model reaction of methyl acetate and anhydrous ethanol. The use of this model reaction is very useful at this initial step of investigation, in the screening of the active catalysts for transesterification. The model reaction is easier to perform than the reaction involving the triglyceride (vegetable oil) to produce biodiesel and the products are quickly monitored by gas chromatography (4 min run). In addition, the stability tests can be properly carried out when using the model compounds. It is noteworthy that ethanol has been chosen as the alcohol source due to its renewable origin.

The catalytic tests were performed in the low conversion regime in order to better distinguish the catalytic activity. The tests were carried out in a batch jacket reactor of volumetric capacity of 30 mL using magnetic stirring under the following conditions: mol ratio of ethanol/methyl acetate = 6/1, 0.2 wt.% of catalyst and temperature of 313 K. Representative aliquots of the solution were withdrawn periodically and submersed in an ice bath. The solid catalysts were separated by centrifugation and the reaction products analyzed in a gas chromatograph (GC 2010 Shimadzu) equipped with FID and RTx®-1 capillary column.

2.4. Stability tests

Chemical analysis of the reaction mixture was performed in order to verify the possible lithium leaching from the catalysts to solution. The lithium content in the reaction mixture was analyzed by SPE-CAA100 Varian flame emission spectrometer. The procedure consisted of solution filtration at the end of the reaction in order to remove the solid catalyst by using syringe filters (0.45 μm pore size). Thus, an aliquot of 1 mL of the filtrate composed of volatile compounds was evaporated and the residual metals were resuspended with HNO$_3$ (1% v/v) solution for the chemical analysis. The material stabilities were also investigated by the catalyst reaction with ethanol in order to determine the homogeneous contribution. The catalysts were stirred in ethanol for 150 min at 313 K and filtered. This filtered ethanol was used for transesterification of the methyl acetate. The solution composition was monitored afterwards.

3. Results and discussion

3.1. Structural, textural and chemical characterization of the catalysts

XRD analyses for the materials are presented in Fig. 1. The XRD for Mg(OH)$_2$ confirmed the formation of brucite structure
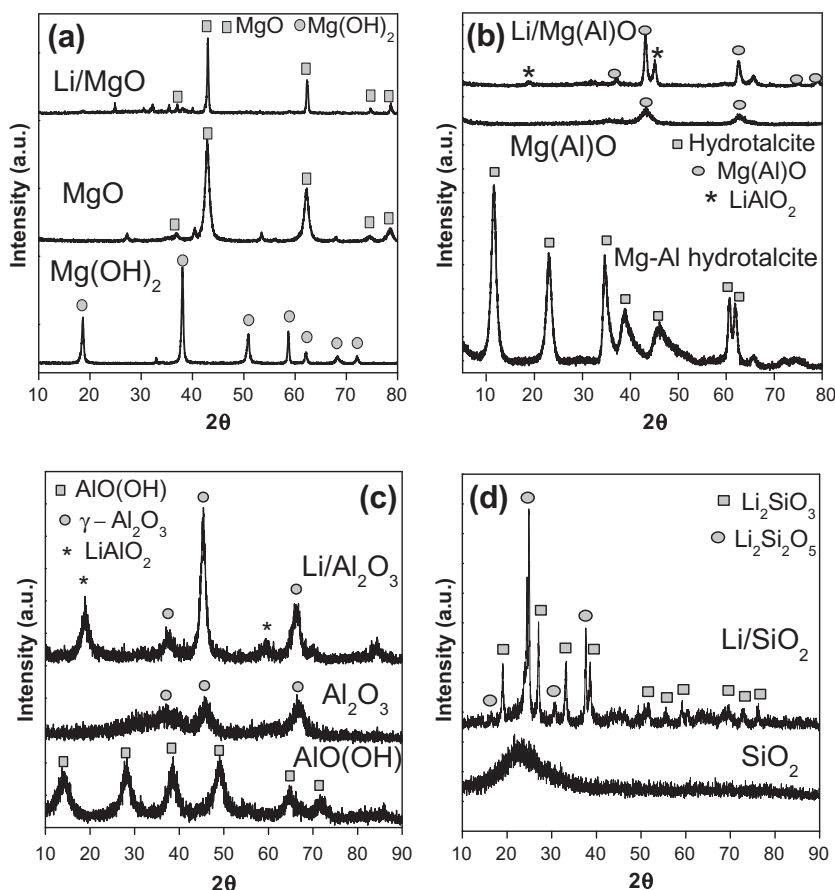
Fig. 1. XRD for the precursor of the support, supports and Li-based oxides.

$(Mg(OH)_2)$ [JCPDS 76-0667]. This phase was converted into MgO [JCPDS 87-0652] after calcination. The Li/MgO showed an MgO structure and no Li_2O diffractions were detected (Fig. 1a). This suggests that Li_2O, expected to be formed from $LiNO_3$ decomposition, is in small particle size and evenly dispersed over the MgO matrix. Actually, no Li_2O diffractions were detected for all Li containing samples which was also found in previous reports for MgO supported Li [15], ZnO supported Li [17] and CaO supported Li [13]. Another possible explanation for the absence of diffractions related to lithium compounds is the MgO doping with Li. The ionic radii of Li^+ ($r_{Li+} = 0.76$ Å) is close to that of Mg^{2+} ($r_{Mg2+} = 0.72$ Å), so allowing the replacement of Mg^{2+} by Li^+ in the MgO structure [18].

The XRD for MgAl hydrotalcite showed characteristic diffractions of the hydrotalcite structure [JCPDS 22-0700]. After calcination, an Mg(Al)O mixed oxide of low crystallinity with MgO periclase-type structure is obtained [JCPDS 75-1525]. The Mg(Al)O acronym is used to denote that the Al^{3+} cations are highly dispersed in the MgO lattice without segregation of crystalline phases of AlOx. Fig. 2 gathers the XRD for MgO and Mg(Al)O. Indeed, the addition of Al^{3+} into MgO caused diffraction shifts towards higher 2θ values and this is a consequence of the MgO lattice contraction in the presence of Al^{3+} (ionic radii: $r_{Mg2+} = 0.72$ Å and $r_{Al3+} = 0.54$ Å). The lattice parameter for MgO was $a = 4.219$ Å whereas for Mg(Al)O it was $a = 4.187$ Å, suggesting that the Al^{3+} cations from Mg(Al)O are replacing the Mg^{2+} cations in the MgO structure [19,20].

The Li/Mg(Al)O sample showed to be composed of MgO and likely $LiAlO_2$ [JCPDS 44-0224] (Fig. 1b). The alumina precursor was identified as boehmite, AlO(OH) [JCPDS 05-0190] which was converted after calcination into a γ-Al_2O_3 of low crystallinity as evidenced by the broad diffraction lines [JCPDS 01-1303]. The

Li/Al_2O_3 showed diffractions ascribed to γ-Al_2O_3 [JCPDS 01-1303] and $LiAlO_2$ [JCPDS 44-0224] (Fig. 1c). The commercial SiO_2 "impregnated" only with distilled water and calcined (reference sample) presented typical amorphous structure. Impregnation of $LiNO_3$ onto SiO_2 followed by calcination led to a mixture of lithium metasilicate Li_2SiO_3 [JCPDS 15-0519] and lithium disilicate $Li_2Si_2O_5$ (or Li_2O $2SiO_2$) [JCPDS 14-0322]. The formation of silicate phases indicates the reaction between Li_2O and SiO_2 forming stable compounds (Fig. 1d).

By observing the XRD for the Li containing samples, one can realize clearly that the Li addition markedly increased the oxide
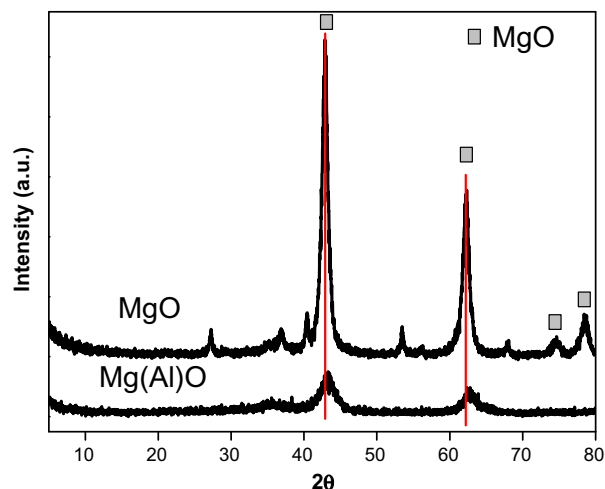

Fig. 2. XRD for MgO and Mg(Al)O oxides.

Table 1
BET surface area, crystallite size and chemical analysis of the catalysts.

Catalyst	BET surface area (m^2/g)	Crystallite size (nm)	Lithium loading (wt.%)[a]
MgO	135	9.2	–
Li/MgO	13	37.1	4.7 ± 0.1
Mg(Al)O	201	2.6	–
Li/Mg(Al)O	5	25.0	4.9 ± 0.1
Al$_2$O$_3$	304	36.2	–
Li/Al$_2$O$_3$	130	n.d.[b]	7.7 ± 0.2
SiO$_2$	252	n.d.[c]	–
Li/SiO$_2$	119	n.d.[c]	8.2 ± 0.2

[a] Obtained by ICP–OES.
[b] Not determined due to the overlapping peaks ascribed to γ-Al$_2$O$_3$ and LiAlO$_2$.
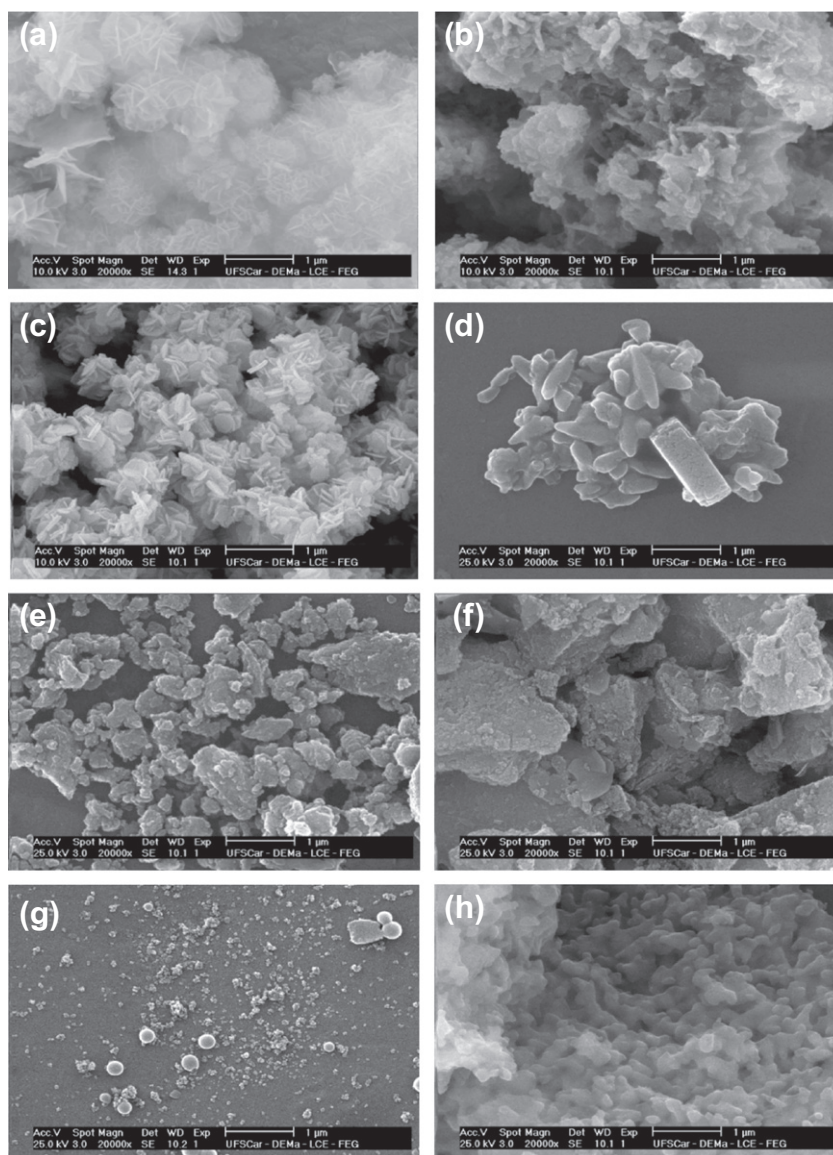[c] Not determined due to the amorphous nature of silica.

Fig. 3. Field-emission scanning electron micrographs (FEG-SEM) of the Mg(Al)O (a); Li/Mg(Al)O (b); MgO (c); Li/MgO (d); γ-Al$_2$O$_3$ (e); Li/Al$_2$O$_3$ (f); SiO$_2$ (g) and Li/SiO$_2$ (h).

crystallinities, showing more intense and narrower diffraction peaks than the oxides without Li (Fig. 1). This result reflects the growth of the crystallites [21]. For example, the MgO crystallite size calculated by Scherrer equation using its main diffraction peak (2θ = 43.0°) was 9.2 nm whereas for Li/MgO was 37.1 nm (Table 1).

The crystallite size increase is a consequence of the thermal stability reduction of the Li containing oxides. It is reported in the literature that some alkali metals are able to distort the oxide structures upon heating, causing sintering [18,21,22]. The sintering effect causes the particle growth and decreases the solid surface
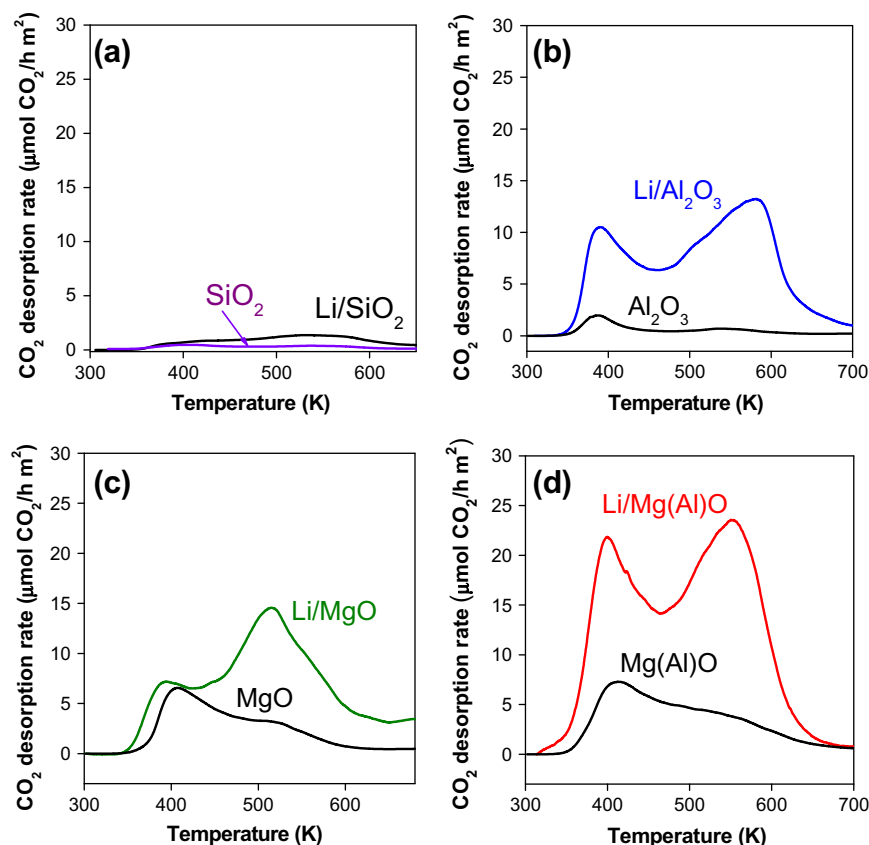
Fig. 4. TPD of CO_2 profiles on the supports and lithium based catalysts.

areas. Indeed, as can be seen from the data in Table 1, the Li addition onto the oxides reduced the surface area of all materials. The surface area reduction was more significant for Li/MgO and Li/Mg(Al)O than for Li/Al$_2$O$_3$ and Li/SiO$_2$.

Table 1 also presents the Li catalysts loading obtained by ICP–OES. It can be observed that the Li loadings were lower than the nominal values of 10 wt.% Li for all catalysts. This is probably due to the Li loss at the impregnation step and/or mainly by Li$_2$O evaporation during the catalyst calcination at the high temperature of 873 K [18,23].

In order to investigate the effect of the Li addition on the catalyst morphology, representative samples were studied by FEG-SEM. Fig. 3a shows the platelet structure of Mg(Al)O, typical for mixed oxides obtained from hydrotalcite precursor [24–26]. The MgO (Fig. 3c) presents a flake-like morphology [15,27] whereas γ-Al$_2$O$_3$ (Fig. 3e) exhibits irregular clod core forms [28,29]. In the case of silica (calcined Aerosil$^®$380) (Fig. 3g), spherical particles can be clearly observed.

For the Li containing oxides (Fig. 3b and d, f and h), considerable morphological changes have occurred, leading to oxides with a smoother appearance, larger particle size and round corners. These findings are consistent with the sintering effect detected by XRD and also the surface area reduction after Li addition onto the catalysts.

The temperature-programmed desorption of CO_2 (TPD of CO_2) was used to evaluate the base properties of the catalysts. Fig. 4 presents the CO_2 desorption rate for the oxides and Li-based catalysts.

No CO_2 desorption signal was detected for SiO$_2$ (Fig. 4a) whereas γ-Al$_2$O$_3$ (Fig. 4b) revealed to be mainly composed of weak base sites that desorbed CO_2 at low temperature range (<400 K). The γ-Al$_2$O$_3$ is an amphoteric oxide whose base sites are ascribed primarily to surface –OH groups [30,31].

In the case of MgO (Fig. 4c) and Mg(Al)O obtained from hydrotalcite (Fig. 4d), it is well known that they are comprised of three types of base sites: (i) surface hydroxyl groups (–OH), (ii) Lewis acid-Bronsted base pairs (M^{n+}–O^{2-} being M^{n+} the metal cation Mg^{2+} or Al^{3+}) and (iii) isolated surface O^{2-} anions of low-coordination from the corners or edges of the crystal lattice. These surface oxygen species possess the following base strength order: O^{2-} anions > metal–oxygen (M^{n+}–O^{2-}) pairs > hydroxyl groups [14,32].

It is apparent from Fig. 4 that the Li addition onto the oxides caused a marked increase in the base site densities, observed by the area under the TPD curves. This effect was less noticeable for Li/SiO$_2$ (Fig. 4a). Lithium also changed the base strength distribution revealed by the different shapes of the TPD curves (Fig. 4b–d) [33]. A remarkably increase is observed for the strongest base sites with the Li addition and this finding is in agreement with previous work [15].

The total evolved CO_2 was obtained by integration of TPD curves. The TPD of CO_2 profiles were similar for all samples and could be deconvoluted in three desorption peaks with maximum desorption rates at about 388–393 K, 438–488 K and 523–578 K. The contribution of each desorption peak is presented in Table 2.

3.2. Catalytic tests

The catalytic tests were carried out through the model transesterification reaction between methyl acetate and ethanol. All the oxides (MgO, γ-Al$_2$O$_3$, Mg(Al)O, and SiO$_2$) and oxide precursors (Mg(OH)$_2$, Al(O)OH, MgAl hydrotalcite and Aerosil$^®$380) were inactive for transesterification. In contrast, the Li addition onto the oxides increased markedly its catalytic activity. Fig. 5 displays the transesterification in the presence of the Li-based catalysts.

Table 2
Density of base sites of the lithium based catalysts.

Catalysts	Density of base sites – nb ($\mu mol/m^2$)			
	Total nb[a]	Weak nb	Medium nb	Strong nb
Li/SiO$_2$	0.4	0.0	0.1	0.3
Li/Al$_2$O$_3$	4.5	0.9	1.8	1.8
Li/MgO	3.3	0.6	0.2	2.5
Li/MgAl	7.3	1.0	2.4	3.9

[a] nb = number of base sites.

It is interesting to note that the nature of the support strongly influenced the activity of the Li-based catalysts. Low conversion to products was obtained for Li supported onto SiO$_2$ and γ-Al$_2$O$_3$. Possibly, the Li$_2$O formed during LiNO$_3$ heat treatment reacted irreversibly with silica and alumina supports resulting in the stable lithium silicate and lithium aluminate compounds detected by XRD. Thus, the strong interaction between Li$_2$O and SiO$_2$ or γ-Al$_2$O$_3$ can be the cause of the low activity obtained for Li/SiO$_2$ and Li/Al$_2$O$_3$. On the other hand, Li/MgO and Li/Mg(Al)O revealed to be very active under the mild reaction conditions employed in this work. The active site for transesterification may be the highly basic Li$_2$O. Furthermore, the distinctive behavior of Li/MgO can be explained by MgO doping with Li [15]. The replacement of Mg^{2+} by Li$^+$ result in the structural promotion of the MgO lattice and leads to the formation of isolated low coordination O^{2-} anions of high base strength [14]. As reported previously by Berger et al. [18] and Trionfetti et al. [34], the Li$^+$ anions tend to situate on the surface/near-surface region of the MgO crystallites after thermal treatment. They generate defects that are of a great importance for heterogeneous catalysis.

In addition, it should be evidenced that Li/Mg(Al)O was even more active than Li/MgO (Fig. 5). Based on this result, it can be deduced that the incorporation of low amounts of Al^{3+} into MgO (producing the Mg(Al)O) has a positive effect on the creation of the active sites after Li impregnation. According to Di Cosimo et al. [32], the addition of Al^{3+} into MgO creates defects within the MgO lattice and the adjacent oxygen anions become coordinatively unsaturated. Therefore, the Li addition onto an oxide containing structural defects like the Mg(Al)O seems to favor the creation of the active sites for Li/Mg(Al)O even more, resulting in the higher conversion obtained for this sample.

3.3. Catalyst stability: lithium leaching and homogeneous contribution

The catalyst stability was investigated by chemical analysis of the solution after reaction by atomic emission spectroscopy (EAS). Leached lithium was detected in the reaction mixture with concentrations of 0.3 mg L^{-1} of Li$^+$ for Li/SiO$_2$; 1.9 mg L^{-1} when
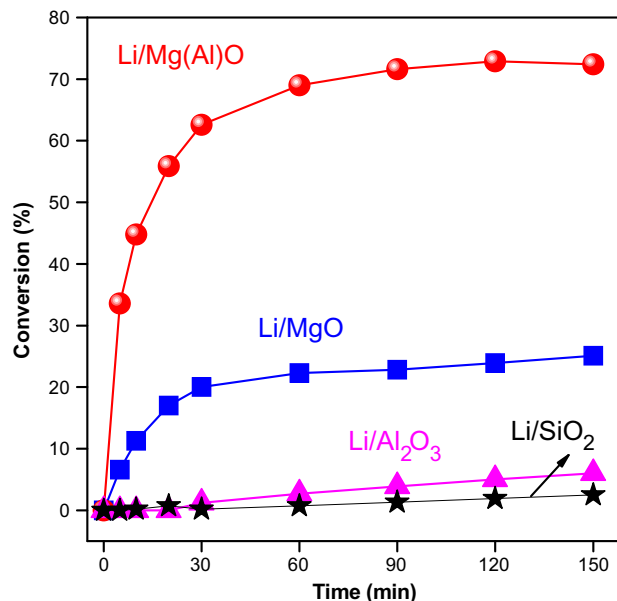
Fig. 5. Catalytic tests for the Li-based catalysts for transesterification reaction between methyl acetate and ethanol (313 K, 0.2 wt.% of catalyst, ethanol/methyl acetate molar ratio = 6/1).

using Li/Al$_2$O$_3$; 67.5 mg L^{-1} in the case of Li/MgO and 55.4 mg L^{-1} in the presence of Li/Mg(Al)O.

Frequently, metal leaching is a problem in many supported catalysts. On account of the fact that lithium leached from the Li-based catalysts was detected in the reaction medium, it is important to evaluate the activity of this leached lithium. In general, the leached activity test is not reported in much of the literature concerning heterogeneous catalysts for biodiesel production. The catalyst must be stable to be industrially useful.

If the leached Li$^+$ is inactive for transesterification then the catalysis is truly heterogeneous. However, if the dissolved Li$^+$ is catalytically active then the catalysis is, at least, in part homogeneous. Considering this, the catalyst stability was also investigated by the catalyst reaction with ethanol in order to determine the homogeneous contribution. The tests were carried out in the presence of the samples that presented the highest transesterification activity: Li/MgO and Li/Mg(Al)O. These samples also exhibited the highest lithium leaching. Fig. 6 compares the transesterification in the presence of the solid catalyst and the reaction carried out using the recovered ethanol in contact with methyl acetate.

It can be observed that the leached lithium was active for transesterification (Fig. 6). Therefore, the catalysis is not entirely heterogeneous in the case of Li/MgO and Li/Mg(Al)O. Consequently, the stability of these catalysts should be improved in
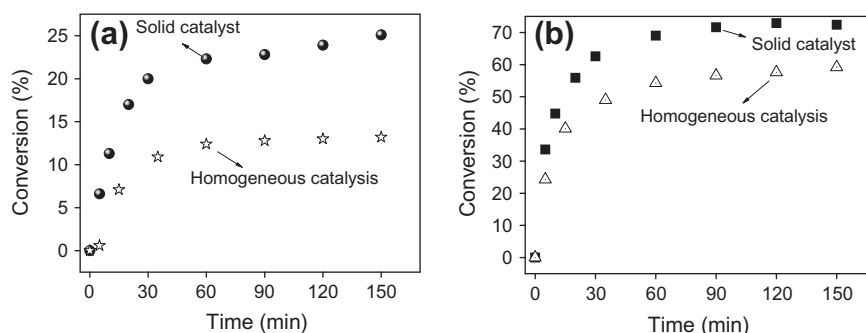
Fig. 6. Transesterification in the presence of the solid catalyst and activity of the leached lithium (homogeneous catalysis) for Li/MgO (a) and Li/Mg(Al)O (b).

order to become suitable for industrial use. Research is currently underway to test further samples.

4. Conclusions

Lithium-based catalysts have been prepared by impregnation of $LiNO_3$ onto supports of different acid/base properties. The Li addition onto MgO, γ-Al_2O_3, Mg(Al)O and SiO_2 causes morphological modifications of the oxides, surface area reduction and increases their crystallite size. However, Li induces changes in the surface reactivity by increasing the number and strength of the base sites. The support nature considerably influences the catalytic performance of the Li-based oxides for transesterification. The strong interaction between Li and γ-Al_2O_3 and SiO_2 supports produces inactive catalysts. On the other hand, Li/MgO and Li/Mg(Al)O are effective catalysts for transesterification. This can be ascribed to the presence of Li_2O along with large amounts of strong basic sites (low coordination O^{2-} sites) in these samples. Remarkably high conversions were found for Li/Mg(Al)O. Therefore, Li/MgO and Li/Mg(Al)O appear to be promising candidates to replace conventional homogeneous catalysts for biodiesel production due to their high transesterification activity at such a low temperature of 313 K. Nevertheless, the Li leaching from the catalysts to solution was detected, and this resulted in some homogeneous contribution. Indeed, the catalyst stability should be improved in order to produce suitable catalysts for biodiesel production.

Acknowledgements

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