Fuel 103 (2013) 632-638

Contents lists available at SciVerse ScienceDirect

Fuel



journal homepage: www.elsevier.com/locate/fuel

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

Cínthia S. Castro^{a,*}, Cristián Ferreti^b, Juana Isabel Di Cosimo^b, José Mansur Assaf^a

^a Chemical Engineering Department, Federal University of São Carlos, Rodovia Washington Luís, Km 235, CEP 13565-905, São Carlos, SP, Brazil ^b Catalysis Science and Engineering Research Group (GICIC), Santiago del Estero 2654, 3000 Santa Fe, Argentina

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

Article history: Received 4 April 2012 Received in revised form 14 June 2012 Accepted 15 June 2012 Available online 29 June 2012

Keywords: Mixed oxides Lithium-based catalysts Heterogeneous catalysis Transesterification Biodiesel

ABSTRACT

Solid catalysts comprising Li-based oxides were prepared by LiNO₃ impregnation onto supports with different acid/base properties (SiO₂, MgO, Al₂O₃ and Mg(Al)O mixed oxide obtained from hydrotalcite). The materials were characterized by means of XRD, N₂ physisorption, ICP–OES, FEG–SEM and TPD of CO₂. 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 transe-sterification. 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.

© 2012 Elsevier Ltd. All rights reserved.

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–La₂O₃ and CaO–La₂O₃ [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].



^{*} Corresponding author. Tel.: +55 16 3351 8047; fax: +55 16 3351 8266. E-mail address: cicastro14@yahoo.com.br (C.S. Castro).

^{0016-2361/\$ -} see front matter @ 2012 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.fuel.2012.06.072

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 -Al₂O₃ and a mixed oxide containing both Mg and Al obtained from hydrotalcite precursor. Furthermore, commercial SiO₂ 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(NO₃)₂·6H₂O and 7.5 g of $Al(NO_3)_3$.9H₂O with Al/(Al + Mg) = 0.2 was added dropwise into another solution containing 2.4 mol L⁻¹ of (NH₄)₂CO₃ under vigorous stirring. The pH during the synthesis was held at 10 by the addition of NH₄OH (30% v/v). The precursors of the Al₂O₃ 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, LiNO₃ was dissolved into 20 mL of distilled water and placed in contact with an appropriated amount of the support precursor, i.g., boehmite – AlO(OH); brucite – Mg(OH)₂; MgAl hydrotalcite or Aerosil[®]380 – SiO₂. The amount of the support precursors AlO(OH) and Mg(OH)₂ were stoichiometrically calculated to generate the pure oxides: Al₂O₃ and MgO. The Aerosil[®]380 is already composed of pure oxide SiO₂. 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 (LiNO₃ 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 LiNO₃ 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 K α 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 CO₂ (TPD of CO₂). 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 CO₂ adsorption was carried out at room temperature using a gaseous mixture of 3% of CO₂ in N₂ until surface saturation (5 min). Physically adsorbed CO₂ was removed by flushing with N₂ for about 1 h. Thus, the CO₂ desorption was performed by increasing the temperature at a rate of 10 K min⁻¹ until 873 K and the flow containing the desorbed CO₂ passed through a methanation reactor. In this step, the desorbed CO₂ was converted into CH₄ on a Ni/Kieselghur catalyst at 673 K. Therefore, the CO₂ desorption was indirectly quantified by the produced CH₄ 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 μ m pore size). Thus, an aliquot of 1 mL of the filtrate composed of volatile compounds was evaporated and the residual metals were resuspended with HNO₃ (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 Li₂O diffractions were detected (Fig. 1a). This suggests that Li₂O, expected to be formed from LiNO₃ decomposition, is in small particle size and evenly dispersed over the MgO matrix. Actually, no Li₂O 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 Mg²⁺ ($r_{Mg2+} = 0.72$ Å), so allowing the replacement of Mg²⁺ 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 Al³⁺ 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 Al³⁺ into MgO caused diffraction shifts towards higher 2θ values and this is a consequence of the MgO lattice contraction in the presence of Al³⁺ (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 Al³⁺ cations from Mg(Al)O are replacing the Mg²⁺ cations in the MgO structure [19,20].

The Li/Mg(Al)O sample showed to be composed of MgO and likely LiAlO₂ [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 -Al₂O₃ of low crystallinity as evidenced by the broad diffraction lines [JCPDS 01-1303]. The

Li/Al₂O₃ showed diffractions ascribed to γ -Al₂O₃ [JCPDS 01-1303] and LiAlO₂ [JCPDS 44-0224] (Fig. 1c). The commercial SiO₂ "impregnated" only with distilled water and calcined (reference sample) presented typical amorphous structure. Impregnation of LiNO₃ onto SiO₂ followed by calcination led to a mixture of lithium metasilicate Li₂SiO₃ [JCPDS 15-0519] and lithium disilicate Li₂SiO₂ (or Li₂O 2SiO₂) [JCPDS 14-0322]. The formation of silicate phases indicates the reaction between Li₂O and SiO₂ 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_2O_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 -Al₂O₃ and LiAlO₂.

^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 -Al₂O₃ (e); Li/Al₂O₃ (f); SiO₂ (g) and Li/SiO₂ (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 $(2\theta = 43.0^{\circ})$ 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 CO₂ 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/Al₂O₃ and Li/SiO₂.

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 Li₂O 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 -Al₂O₃ (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 CO₂ desorption signal was detected for SiO₂ (Fig. 4a) whereas γ -Al₂O₃ (Fig. 4b) revealed to be mainly composed of weak base sites that desorbed CO₂ at low temperature range (<400 K). The γ -Al₂O₃ 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 -Al₂O₃, Mg(Al)O, and SiO₂) 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 2Density 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 SiO₂ and γ -Al₂O₃. Possibly, the Li₂O formed during LiNO₃ 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_2O and SiO_2 or γ -Al₂O₃ can be the cause of the low activity obtained for Li/SiO₂ and Li/Al₂O₃. 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 Li₂O. 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 Al³⁺ 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 Al³⁺ into MgO creates defects within the MgO lattice and the adjacent oxygen anions become coordinatively unsatured. 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/SiO₂; 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/Al₂O₃; 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 LiNO₃ onto supports of different acid/base properties. The Li addition onto MgO, γ -Al₂O₃, Mg(Al)O and SiO₂ 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 -Al₂O₃ and SiO₂ 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 Li₂O 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

The authors are grateful to CNPq (Brazil) and PRH–ANP (Petrobras) for funding this work.

References

- Bart JCJ, Palmeri N, Cavallaro S. Biodiesel catalysis. In: Bart JCJ, Palmeri N, Cavallaro S, editors. Biodiesel science and technology: from soil to oil. Boca Raton: Woodhead Publishing Limited; 2010. p. 322–85.
- [2] Helwani Z, Othman MR, Aziz N, Fernando WJN, Kim J. Solid heterogeneous catalysts for transesterification of triglycerides with methanol: a review. Appl Catal A 2009;363:1–10.
- [3] Lee D, Park Y, Lee K. Heterogeneous base catalysts for transesterification in biodiesel synthesis. Catal Surv Asia 2009;13:63–77.
- [4] Refaat AA. Biodiesel production using solid metal oxide catalysts. Int J Environ Sci Technol 2011;8:203–21.
- [5] Hanna MA, Isom L. Biodiesel current and future perspectives. In: Pandey A, editor. Handbook of plant-based biofuels. Boca Raton: Taylor & Francis Group; 2009. p. 177–82.
- [6] Kouzu M, Hidaka J. Transesterification of vegetable oil into biodiesel catalyzed by CaO: a review. Fuel 2012;93:1–12.
- [7] Zeng H, Feng Z, Deng X, Li Y. Activation of Mg-Al hydrotalcite catalysts for transesterification of rape oil. Fuel 2008;87:3071–6.
- [8] Xie W, Peng H, Chen L. Calcined Mg–Al hydrotalcites as solid base catalysts for methanolysis of soybean oil. J Mol Catal A: Chem 2006;246:24–32.
- [9] Serio MD, Ledda M, Cozzolino M, Minutillo G, Tesser R, Santacesaria E. Transesterification of soybean oil to biodiesel by using heterogeneous basic catalysts. Ind Eng Chem Res 2006;45:3009–14.

- [10] Babu NS, Sree R, Prasad PSS, Lingaiah N. Room-temperature transesterification of edible and nonedible oils using a heterogeneous strong basic Mg/La catalyst. Energy Fuel 2008;22:1965–71.
- [11] Yan SL, Kim M, Salley SO, Simon KY. Oil transesterification over calcium oxides modified with lanthanum. Appl Catal A 2009;360:163–70.
- [12] Watkins RS, Lee AF, Wilson K. Li–CaO catalysed triglyceride transesterification for biodiesel applications. Green Chem 2004;6:335–40.
- [13] Alonso DM, Mariscal R, Granados ML, Maireles-Torres P. Biodiesel preparation using Li/CaO catalysts: activation process and homogeneous contribution. Catal Today 2009;143:167–71.
- [14] Díez VK, Apesteguía CR, Di Cosimo JI. Acid-base properties and active site requirements for elimination reactions on alkali-promoted MgO catalysts. Catal Today 2000;63:53–62.
- [15] Díez VK, Apesteguía CR, Di Cosimo JI. Aldol condensation of citral with acetone on MgO and alkali-promoted MgO catalysts. J Catal 2006;240:235–44.
- [16] Castro CS, Cardoso D, Nascente PAP, Assaf JM. MgAlLi mixed oxides derived from hydrotalcite for catalytic transesterification. Catal Lett 2011;141:1316–23.
- [17] Xie W, Yang Z, Chun H. Catalytic properties of lithium-doped ZnO catalysts used for biodiesel preparations. Ind Eng Chem Res 2007;46:7942–9.
- [18] Berger T, Schuh J, Sterrer M, Diwald O, Knözinger E. Lithium ion induced surface reactivity changes on MgO nanoparticles. J Catal 2007;247:61–7.
- [19] Crocellà V, Cerrato G, Magnacca G, Morterra C, Cavani F, Cocchi S. The balance of acid, basic and redox sites in Mg/Me-mixed oxides: the effect on catalytic performance in the gas-phase alkylation of m-cresol with methanol. J Catal 2010;270:125–35.
- [20] Bolognini M, Cavani F, Scagliarini D, Flego C, Perego C, Saba M. Heterogeneous basic catalysts as alternatives to homogeneous catalysts: reactivity of Mg/Al mixed oxides in the alkylation of m-cresol with methanol. Catal Today 2002;75:103–11.
- [21] Lunsford JH, Cisneros MD, Hinson PG, Tong Y, Zhang H. Oxidative dimerization of methane over well defined lithium-promoted magnesium oxide catalysts. Faraday Discuss Chem Soc 1989;87:13–21.
- [22] Okamoto M, Kodama H, Shinozaki K. Effect of alkali metal oxide addition on the sinterability of MgO-B₂O₃-Al₂O₃ glass-Al₂O₃ filler composites. J Am Ceram Soc 2008;91:1110-4.
- [23] Norby T, Andersen AG. Electrical conductivity and defect structure of lithium doped magnesium oxide. Appl Catal A 1991;71:89–102.
- [24] Abelló S, Medina F, Tichit D, Pérez-Ramírez J, Rodríguez X, Sueiras JE, et al. Study of alkaline-doping agents on the performance of reconstructed Mg–Al hydrotalcites in aldol condensations. Appl Catal A 2005;281:191–8.
- [25] Greenwell HC, Holliman PJ, Jones W, Velasco BV. Studies of the effects of synthetic procedure on base catalysis using hydroxide-intercalated layer double hydroxides. Catal Today 2006;114:397–402.
- [26] Tittabut T, Trakarnpruk W. Metal-loaded MgAl oxides for transesterification of glyceryl tributyrate and palm oil. Ind Eng Chem Res 2008;47:2176–81.
- [27] Meshkania F, Rezaei M. Nanocrystalline MgO supported nickel-based bimetallic catalysts for carbon dioxide reforming of methane. Int J Hydrogen Energy 2010;35:10295–301.
- [28] Hosseini SA, Niaei A, Salari D. Production of γ-Al₂O₃ from Kaolin. Open J Phys Chem 2011;1:23–7.
- [29] Hosseini Z, Taghizadeh M, Yaripour F. Synthesis of nanocrystalline γ -Al₂O₃ by sol-gel and precipitation methods for methanol dehydration to dimethyl ether. J Nat Gas Chem 2011;20:128–34.
- [30] Di Cosimo JI, Apesteguía CR, Ginés MJL, Iglesia E. Structural requirements and reaction pathways in condensation reactions of alcohols on MgyAlOx catalysts. J Catal 2000;190:261–75.
- [31] Díez VK, Di Cosimo JI, Apesteguía CR. Study of the citral/acetone reaction on MgyAlOx oxides: effect of the chemical composition on catalyst activity, selectivity and stability. Appl Catal A 2008;345:143–51.
- [32] Di Cosimo JI, Díez VK, Apesteguía CR. Synthesis of α, β-unsaturated ketones over thermally activated Mg-Al hydrotalcites. Appl Clay Sci 1998;13:433–49.
- [33] Ferretti CA, Soldano A, Apesteguía CR, Di Cosimo JI. Monoglyceride synthesis by glycerolysis of methyl oleate on solid acid-base catalysts. Chem Eng J 2010;161:346–54.
- [34] Trionfetti C, Babich IV, Seshan K, Lefferts L. Presence of lithium ions in MgO lattice. Surface characterization by infrared spectroscopy and reactivity towards oxidative conversion of propane. Langmuir 2008;24:8220–8.