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Biodiesel preparation using Li/CaO catalysts: Activation process and homogeneous contribution

D. Martín Alonso [a,*], R. Mariscal [a], M. López Granados [a], P. Maireles-Torres [b]

[a] Instituto de Catálisis y Petroleoquímica, CSIC, C/Marie Curie 2, Campus de Cantoblanco, E-28049, Madrid, Spain
[b] Departamento de Química Inorgánica, Cristalografía y Mineralogía (Unidad Asociada al ICP-CSIC), Facultad de Ciencias, Universidad de Málaga, Campus de Teatinos, 29071 Málaga, Spain

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ABSTRACT

This work studies the influence of the lithium content and activation temperature of Li-doped CaO catalysts in the transesterification reaction of triglycerides with methanol and the homogeneous contribution. Several samples with different lithium content have been studied, and a lithium concentration >3.6 wt% of lithium was expected to exert a promoter effect. The influence of activation temperature has been investigated for 4.5LiCa catalyst, requiring a temperature of activation above the melting point of $LiNO_3$ (492 K) to observe any catalytic activity. Moreover, it has been observed that the homogeneous contribution, and consequently the amount of lithium species leached, depends on activation temperature: the leaching of lithium and homogeneous contribution is significant for activation temperatures ≥973 K (87% in 3 h), when Li oxides was present in the sample, whereas the homogeneous contribution is little relevant at activation temperatures ≤773 K, where $LiNO_3$ has not yet decomposed. Consequently at activation temperatures between 773 and 973 K, an intermediate situation, will be expected.

1. Introduction

The global production of biodiesel is growing sharply. Biodiesel can substitute conventional diesel, being a non-toxic and biodegradable fuel considered to be environmentally friendly and renewable. It is produced from vegetable oils by the transesterification of triglycerides with methanol in the presence of a catalyst to yield the corresponding fatty acid methyl esters (FAME) and glycerol as co-product. Current technology uses a homogeneous basic catalyst (NaOH or KOH dissolved in methanol, a corrosive liquid).

Although the homogeneous catalyzed biodiesel reaction is relatively fast and records high conversions, it has some serious drawbacks. The catalyst cannot be recovered and it must be neutralized and separated from the methyl ester phase at the end of the reaction, with the consequent generation of a large volume of wastewater. Heterogeneous basic catalysts could solve these issues; they could be easily separated from the reaction mixture by filtration and reused. They are less corrosive, meaning safer, cheaper and more eco-friendly operation.

Bulk CaO has been identified as a promising active and reusable catalyst in the transesterification reaction, where the activation process and particle size have been reported as essential points for its catalytic performance [1–4]. In order to improve this behaviour, CaO has been supported on a mesoporous catalyst [5] and coprecipitated with other metals as zinc oxide [6] to increase its dispersion. However, another strategy to increase CaO catalytic activity could be to promote it with alkaline metals. Since it is known that Li salts increase the basicity of MgO [7], one reasonable strategy to increase the activity of CaO could be its promotion with this alkaline metal because a correlation has been reported between the basicity of surface centres and transesterification activity [8].

Pioneering work by Watkins et al. [8] reported the incorporation of $LiNO_3$ on CaO catalyst. They varied the $LiNO_3$ amount and showed a promoter effect on the transesterification of glyceryl tributyrate and methanol to methyl butanoate. Recently, Meher et al. [9,10] have reported that Li/CaO is a promising heterogeneous catalyst for biodiesel production and that its performance was not significantly affected by the presence of a high FFA content up to 5.75%. The optimization of reaction conditions was also investigated. However, leaching and homogeneous contributions were not studied. More recently, Shumaker et al. [11,12] have reported that the Li–Al laminar catalyst is active in the transesterification of

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* Corresponding author. Tel.: +34 915 854 942; fax: +34 915 854 760.
E-mail address: davidm@icp.csic.es (D.M. Alonso).

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vegetable oil, but they conclude that much longer operation times are required to evaluate the catalyst stability and determine whether lithium leaching is a serious issue. Xie et al. [13] have studied Li/ZnO catalysts, specifically aspects like the lithium content and activation process, showing that catalyst activity for the transesterification reaction is closely related to their basic properties. MacLeod et al. [14] have evaluated the stability of alkali-doped metal oxide catalysts for application to biodiesel production, concluding that metal leaching from the catalyst was detected, and this resulted in some homogeneous activity. This drawback would need to be resolved before scaling-up biodiesel production.

Despite these studies, aspects like the explication of the Li effect, the homogeneous contribution and the leaching of lithium species remains unclear. The aim of this work is to clarify this controversy; the influence of the lithium amount has been studied, but focusing also on the effect of activation process on the catalytic performance and the homogeneous contribution by leached species. In particular, the influence of the activation temperature of 4.5LiCa promoted catalyst on the catalytic activity has been evaluated.

2. Experimental

2.1. Preparation of catalysts

A series of catalysts was prepared to study the promoter effect of the lithium supported on CaO. Samples with different amounts of lithium were prepared by wet impregnation method with lithium nitrate (99.98% metal basic, Alfa Aesar) previously dissolved in 5 mL of deionised water per gram of CaO (99.9% metal basis, Aldrich). The amount of lithium salt was selected to obtain 1.2, 2.4, 3.6, 4.5 and 6.0 wt% lithium. The percentages in weight correspond to the catalysts after activation. It was assumed that the activation temperature was enough to decompose lithium nitrate salt to give Li_2O, although as it will be shown later this is not necessarily true and will depend on the activation temperature. The mixture was stirred in a rotavapour for 2 h. Water was then removed at a pressure of 200 mmHg and a temperature of 343 K. The solids were dried in an oven at 393 K overnight to obtain the corresponding precursors. A CaO sample, used as a reference, was obtained with the same procedure but using pure deionised water. Lithium nitrate was selected as precursor because it is not expensive and its solubility in water is very high. These catalysts were activated under inert gas flow at the selected temperature. The catalysts have been labelled as *x*LiCa, where *x* is the weight percentage of lithium.

2.2. Activity measurements

The transesterification reaction of commercial food-grade sunflower oil was carried out in a 100 mL jacketed three-necked glass reactor with a condenser and a dropping funnel. Anhydrous methanol (Riedel-de Häen) was placed in contact with the activated solid, avoiding contact between the catalyst and the ambient atmosphere, and the temperature of the methanol-solid mixture was raised to 333 K. The mixture was kept under an inert atmosphere of nitrogen. The reaction started when preheated sunflower oil at 333 K was added to the reactor through the dropping funnel. This three-phase system was vigorously stirred (1000 rpm). The weight of methanol and oil loaded in the reactor was 27.0 g and 50 g, respectively, (methanol:oil molar ratio of 14:1) plus 100 mg of catalyst, which means 0.2 wt% referred to vegetable oil. The reaction was conducted at atmospheric pressure for 3 h. Aliquots were extracted by a syringe for sampling analysis, neutralized with 0.1 M HCl to stop the reaction, and the resulting solution was washed with dichloromethane. The alcohol phase (water, glycerine and methanol in excess) was separated from the organic phase (dichloromethane and methyl esters) by decantation, and the residual dichloromethane in the methyl ester phase was finally removed by evaporation. Once the methyl esters had been purified, quantitative analysis was carried out following the European regulated procedure EN 14103; more details can be found elsewhere [3].

2.3. Characterization techniques

The elemental analysis of the samples has been carried out in an ICP-MS Elan 6000 Perkin–Elmer Sciex. Nitrogen adsorption isotherms was recorded at the temperature of liquid nitrogen (77 K), using a Micromeritics ASAP 2000 apparatus for the step-by-step increase of the N_2 dosing pressure to a relative pressure $P/P_0 = 1$. Once the adsorption branch has been completed, the desorption process was followed by steeply decreasing the N_2 relative pressure P/P_0. Samples were degassed following the same procedure as activation in each case prior to the recording of the isotherms. Thermogravimetric analyses were performed in a Mettler Toledo TGA/SDTA 851 operating under inert flow with a heat rate of 10 K min^{-1}. Evolved gas analysis at programmed temperature by mass spectrometry (EGA-MS) was also carried out. The main molecules, such as H_2O, NO, O_2 and CO_2, were monitored by recording the $m/z = 18$, 30, 32 and 44 signals, respectively. 50 mg of the sample was loaded in a U-shaped quartz microreactor and 80 mL (STP) min^{-1} of Ar were passed through while the sample was heated at 10 K min^{-1}. A quadrupole mass spectrometer, model BALZERS Prisma QMS 200 controlled by BALTZER Quadstar^{TM} 422 software, was connected on-line to the reactor outlet for the analysis of generated gases. Powder X-ray diffraction (XRD) patterns were recorded in the 20°–80° range in the scan mode (0.02°, 1 s) in a Siemens D5000 automated diffractometer over a 2θ Brag-Brentano geometry, using Cu K_α radiation and a graphite monochromator. Samples were activated in situ at the indicated temperature under inert flow, and the diffraction patterns were recorded at these temperatures.

3. Results and discussion

3.1. Effect of lithium amount

Fig. 1 shows the FAME yield obtained with the Li/CaO catalysts, activated at 973 K for 2 h, as a function of the lithium content. This activation temperature was selected according to the best results previously obtained for the CaO sample [3]. This temperature allows comparing doped catalyst with the best performance of the reference CaO and hence to infer a possible promoter effect. Three aspects can be inferred from this figure: (i) CaO catalyst impregnated with distilled water without lithium and used as reference (0LiCa sample) reaches a 90% yield after 2 h of reaction; (ii) low amounts of Li (1.2LiCa and 2.4LiCa samples) deactivates the CaO catalyst, giving rise to conversion lower than 5% after 3 h; and (iii) Li percentages higher than 3.6 wt% increase the activity in comparison with the Li-bare catalyst, especially at short contact time. Moreover, all these more active samples reach a high FAME yield.

The chemical analyses of the precursors are included in Table 1. It can be observed that experimental Li loadings are very close to the theoretical ones, so it can be concluded that lithium is present in all the samples. No lithium losses were observed after the activation process.

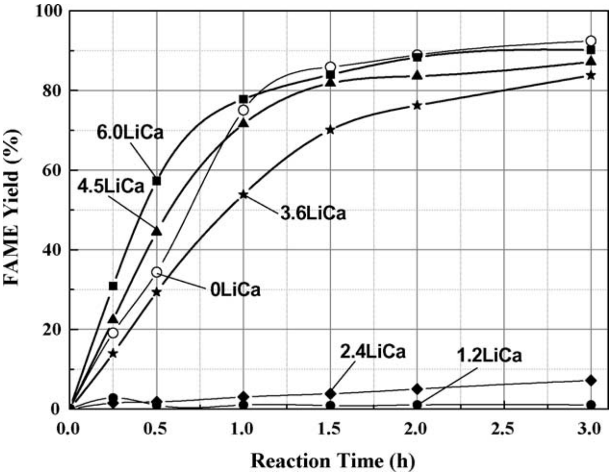

Fig. 1. FAME yield of the different LiCa catalysts activated at 973 K.

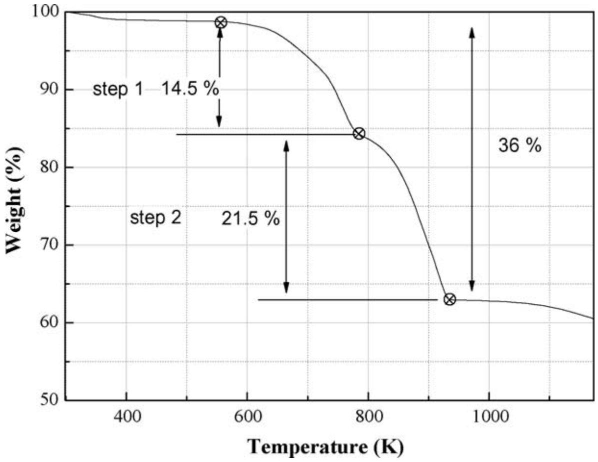

Fig. 2. Thermogravimetric analysis of the 4.5LiCa catalyst under nitrogen flow.

XRD data were carried out. In all cases diffraction patterns correspond to cubic CaO phase, after activation in inert atmosphere at 973 K, and no Li containing phases were detected (diffraction patterns are not shown here). Similar observations have been previously reported [13,15]. The fact that lithium oxide has not been observed could be due to the lower scattering factor for Li than for CaO or the low amounts of lithium added. The fact that samples with low amounts of Li are inactive has been previously observed by Watkins et al. when CaO is promoted with $LiNO_3$ [8]. They have found that increasing the amount of promoter, the Li^+ ions initially trapped into structural defects of the bulk CaO also appear on the surface of the support. In our case, it is possible that lithium oxide placed in defects of CaO does not improve the superficial basicity of CaO, and a promoting effect is only observed after increasing the amount of lithium.

Concerning the textural properties of this series of catalysts, Li-bare catalyst possesses a high surface area ($30\,m^2\,g^{-1}$) in comparison with Li promoted catalysts ($<1\,m^2\,g^{-1}$), suggesting that the surface sites in the promoted catalysts present a higher intrinsic activity than for CaO, at least for samples with Li percentages higher than 3.6. This fact could be explained by taking into account the higher basicity of Li containing samples; this is well known and has been extensively reported [7–11,14]. However, catalysts with low lithium content whose surface basicity has not been increased are not active due their low specific surface.

As mentioned in the introduction, the main controversial aspect in the literature and one of the most important problems associated to the use of doped CaO is the possibility of leaching of soluble species in the reaction medium and that those species could contribute to the catalytic performance (homogeneous contribution), resulting in non-reusable catalysts. On the other hand the activation temperature is one of the key factors that can influence in the leaching and therefore in the homogeneous contribution. The activation process of sample 4.5LiCa has been investigated in order to study the effect of activation temperature on catalytic activity.

Table 1
Chemical analysis by ICP-MS of Li/CaO precursors (weight relation Li:Ca).

Catalyst	Theoretical Li:Ca	Experimental Li:Ca
0Li	–	–
1.2Li	0.017	0.018
2.4Li	0.036	0.035
3.6Li	0.054	0.058
4.5Li	0.070	0.074
6.0Li	0.096	0.098

3.2. Effect of activation temperature

TG analysis under nitrogen flow of 4.5LiCa is displayed in Fig. 2. Two weight losses are observed: (i) a first loss in the 623–773 K temperature range (14.5%), which is attributed to dehydration of the catalyst; and (ii) a second weight loss (21.5%) associated to the decomposition of the lithium nitrate. A slight weight loss is observed at higher temperatures, possibly due to decarbonation. Moreover, an endothermic peak without weight loss was observed in the differential thermal experiments (profile not shown here)

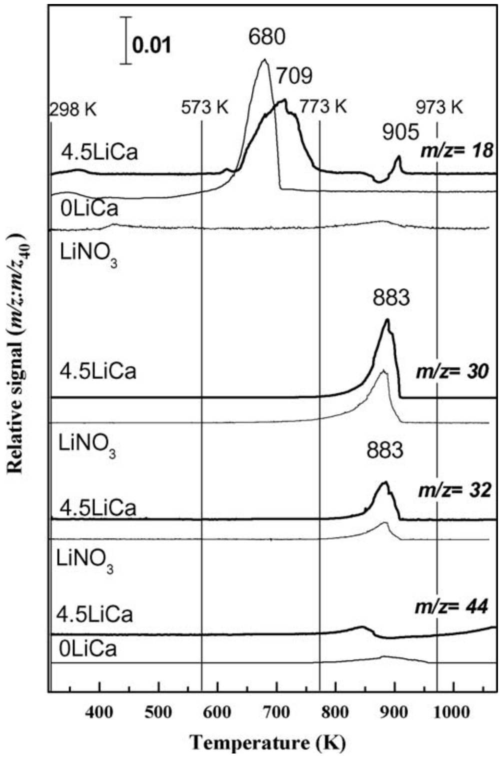

Fig. 3. EGA-MS profiles of the $m/z = 18(H_2O)$, $30(NO)$, $32(O_2)$ and $44(CO_2/N_2O)$ for the 4.5LiCa, 0LiCa and $LiNO_3$ samples under argon flow.

with a maximum at 492 K associated to the melting process of the $LiNO_3$ salt. TG analysis indicates that the precursor is mainly $Ca(OH)_2$. This is expected after using a wet impregnation technique to support $LiNO_3$.

The analysis of the activation process was completed by evolved gas analysis by mass spectrometer (EGA-MS). The 4.5LiCa profiles of the m/z = 18, 30, 32 and 44 are displayed in Fig. 3, which are used to follow the evolution of H_2O, $NO + O_2$ and CO_2, respectively. Moreover, this study has been also carried out for Li-bare catalyst and $LiNO_3$, used as reference. The EGA-MS data also allow us to assign the different steps observed in the TG curves. Thus, it is confirmed that after an initial dehydration process, the decomposition of lithium nitrate and a small contribution at higher temperature due to decarbonation take place. EGA-MS results show that promoted LiCaO samples are barely carbonated. This means that the impregnation procedure prevents the carbonation of CaO and the second weight loss observed in TG analysis can be assigned to the decomposition of $LiNO_3$. According to the TG and EGA-MS experiments, it seems reasonable to select the following activation temperatures for 2 h to study its effect on the catalytic performance: 298 K without any activation process; 573 K, after the melting point of $LiNO_3$ (492 K); 773 K, after the dehydration process and 973 K, after $LiNO_3$ decomposition has been completed (see Fig. 3).

The effect of the activation temperature on the catalytic performance of 4.5LiCa sample is shown in Fig. 4. At 298 K, the precursor is practically inactive (FAME yield lower than 10% after 3 h). By increasing the activation temperature, a FAME yield of 70% is attained at 573 K after the same reaction time. The activation at 773 K results in a very active catalyst, in 1 h of reaction time a yield of 90% is obtained. When the bare CaO is activated at 773 K, only 80% of yield is reached in 1 h, pointing to the existence of a promoter effect of $LiNO_3$ supported on CaO. Curiously, the activity behaviour is worse at a higher temperature (973 K), where decarbonation was completed. Catalyst sintering can be discarded to explain such behaviour, because all the samples have a very low specific surface ($<1\ m^2\ g^{-1}$), so the influence of specific surface can be ruled out. Xie et al. [13] observed the presence of Li_2ZnO_2 mixed oxides after activation at high temperatures. It is possible that the deactivation of the catalyst after activation at high temperatures could be due to the interaction between CaO and Li_2O. To analyse this latter hypothesis, the XRD of the samples activated in situ was carried out.

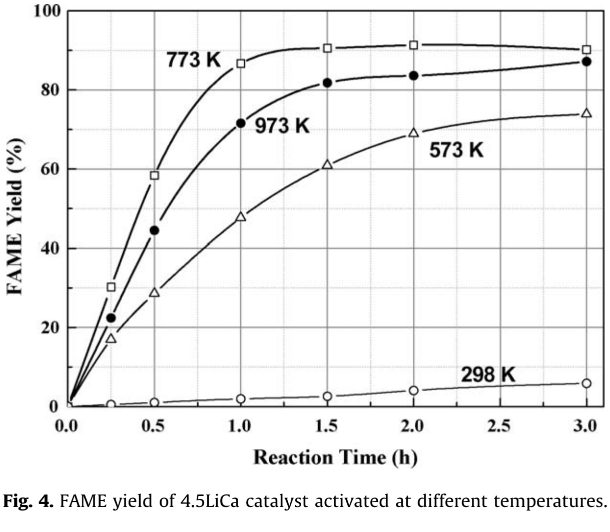

Fig. 4. FAME yield of 4.5LiCa catalyst activated at different temperatures.

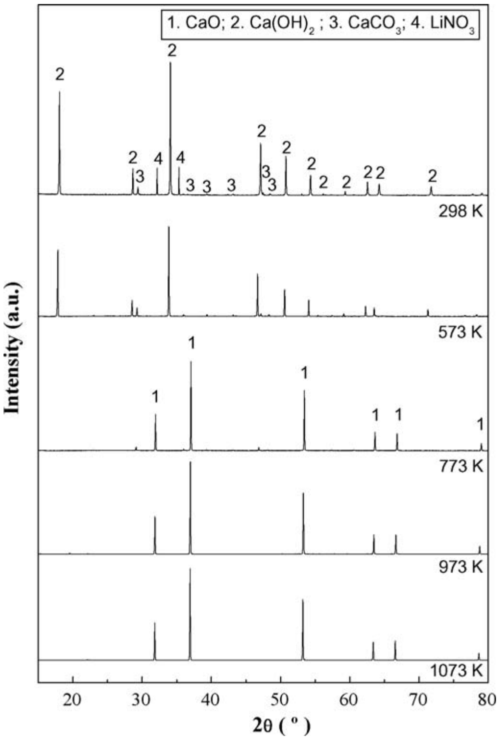

Fig. 5. X-ray patterns of the 4.5LiCa catalyst after its activation at different temperatures.

Fig. 5 shows the XRD patterns of the 4.5LiCa samples. The XRD pattern of non-activated sample only exhibits peaks corresponding to $Ca(OH)_2$ and $LiNO_3$ crystalline phases. This explains the low activity when the catalyst was not activated. It is known that the low basic strength of $Ca(OH)_2$ is not enough to catalyse the transesterification of triglycerides [1], thus suggesting that $LiNO_3$ is unable to increase the basicity of $Ca(OH)_2$. After activation at 573 K, only $Ca(OH)_2$ was observed. At this temperature of activation lithium nitrate has melted out and its crystalline structure has broken down. It seems that after the melting point some chemical reaction between CaO and $LiNO_3$ could occur, promoting the catalyst activity, but this possible new phase has not been detected by XRD. At 773 K, the $Ca(OH)_2$ dehydration process has taken place and the CaO crystallites are clearly observed in the XRD patterns, resulting in the most active catalyst, although a little amount of $Ca(OH)_2$ was still present. The XRD pattern after activation at 973 K is similar to that at 773 K. At 973 K the dehydration and $LiNO_3$ decomposition processes are completed. Only CaO features were observed even at higher activation temperature (1073 K). No mixed oxides between Li and CaO were detected by XRD (see Fig. 5), as in the case of ZnO promoted lithium [13].

3.3. Homogeneous contribution

Homogeneous contribution can be responsible for catalytic activity, as previously observed for K_2O/Al_2O_3 catalysts [16]. In the case of CaO promoted with lithium, two situations should be studied: (i) after activation at 973 K in order to have Li_2O on the surface of CaO and (ii) after thermal treatment at 773 K when lithium is as $LiNO_3$. In situ hot filtration in methanol of 4.5LiCa sample was used to determine the homogeneous contribution. Thus the catalyst was exposed to methanol for 1 h at 333 K and this methanol was filtered out and used to transesterify the sunflower oil. Then the reaction was carried out.

When 4.5LiCa is activated at 973 K, a high FAME yield was obtained (87% in 3 h). Therefore, this catalytic activity should be associated to the leaching of active species from Li_2O and CaO and in a minor extension to the small fraction of solid that goes through the filter. Using the same in situ hot filtration methodology, the FAME yield due to the homogeneous contribution of leaching species from pure CaO and the small fraction of solid CaO that goes through the filter was 5% in 3 h. This reveals that homogeneous contribution due to the presence of Li_2O is significant.

Under the second set of experimental conditions, activation of 4.5LiCa at 773 K, the homogeneous contribution of LiCa catalysts was lower (FAME yield of 22% in 3 h) and should be associated to the leaching of active species from CaO and the little amount of Li_2O that can be formed during the activation process. Since $LiNO_3$ was not active in the transesterification reaction (conversion to methyl esters $<0.5\%$ after 2 h and 1 wt% of catalyst) it cannot be responsible of the activity even if it leaches to the medium.

When the catalyst is activated at 773 K, catalytic activity must be mainly attributed to the heterogeneous process due to the presence of solid CaO promoted with $LiNO_3$. The existence of a promoting effect of $LiNO_3$ on the activity of CaO is more evident if we consider that the amount of CaO in the promoted catalyst is only 80% of the amount present in the CaO (the other 20% is $LiNO_3$ that is not active).

The evaluation of the reutilisation of catalysts is usually employed to get information about the catalyst stability. Nevertheless, this procedure has to be properly carried out. Using low catalyst loading, handling is not easy and an important contribution of catalytic activity reduction may be due to the loss of catalyst rather than active phase leaching. However, when high catalyst amounts are used, reuse experiments do not provide significant information, as catalyst can be reused in various cycles without significant loss in activity and a higher number of runs are required. It is only relevant if the homogeneous contribution is very important [14]. Another option is to reduce the reaction time when the amount of catalyst is increased, but this means reducing contact time between methanol and the catalyst and reducing the extension of active phase lixiviation.

So the apparent contradiction in the different results reported in the literature concerning homogeneous contribution is not as such when two situations should be considered. The homogeneous contribution for Li/CaO catalyst depends on the lithium loading, and mainly on the activation temperature which, in our particular case, can allow the presence of $LiNO_3$ or Li_2O. Therefore, it is evident that complementary characterization is clearly required to understand why catalysts with low amount of lithium are not active and explain the final cause of the promoter effect of $LiNO_3$ supported on CaO catalysts. The use of other lithium precursors (LiOH, Li_2CO_3) will be very useful to understand the catalytic performance. In addition to filtering in hot methanol, the reuse experiments under appropriate conditions (catalyst amount) will also be very useful.

4. Conclusions

A series of catalyst with different amounts of lithium supported on CaO was studied, being required a lithium amount above 4.5 wt% to promote the catalytic activity of CaO in the transesterification of sunflower oil. The activation process was necessary to obtain an active catalyst. The catalyst starts to be active when activation temperature was higher than the melting point of $LiNO_3$ (492 K). Above 773 K, the influence of the activation temperature is not significant for catalytic activity, but it is for homogeneous contribution. When Li_2O has been formed, active species are leached in the reaction medium and catalysis is mainly homogeneous; nevertheless, at lower temperatures when $LiNO_3$ is present on CaO, heterogeneous contribution must be responsible for the activity because any possible $LiNO_3$ leached in the reaction medium is not active. The promoter effect of $LiNO_3$ has been observed in a sample activated at 773 K.

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References

[1] S. Gryglewicz, Bioresour. Technol. 70 (1999) 249.
[2] C. Reddy, V. Reddy, R. Oshel, J.G. Verkade, Energy Fuels 20 (2006) 1310.
[3] M.L. Granados, M.D.Z. Poves, D.M. Alonso, R. Mariscal, F.C. Galisteo, R. Moreno-Tost, J. Santamaria, J.L.G. Fierro, Appl. Catal. B: Environ. 73 (2007) 317.
[4] X.J. Liu, H.Y. He, Y.J. Wang, S.L. Zhu, X.L. Piao, Fuel 87 (2008) 216.
[5] M.C.G. Albuquerque, I. Jimenez-Urbistondo, J. Santamaria-Gonzalez, J.M. Merida-Robles, R. Moreno-Tost, E. Rodriguez-Castellon, A. Jimenez-Lopez, D.C.S. Azevedo, C.L. Cavalcante, P. Maireles-Torres, Appl. Catal. A: Gen. 334 (2008) 35.
[6] C. Ngamcharussrivichai, P. Totarat, K. Bunyakiat, Appl. Catal. A: Gen. 341 (2008) 77.
[7] V.R. Choudhary, S.A.R. Mulla, M.Y. Pandit, S.T. Chaudhari, V.H. Rane, J. Chem. Technol. Biot. 75 (2000) 828.
[8] R.S. Watkins, A.F. Lee, K. Wilson, Green Chem. 6 (2004) 335.
[9] L.C. Meher, M.G. Kulkarni, A.K. Dalai, S.N. Naik, Eur. J. Lipid Sci. Technol. 108 (2006) 389.
[10] A. D'Cruz, M.G. Kulkarni, L.C. Meher, A.K. Dalai, J. Am. Oil Chem. Soc. 84 (2007) 937.
[11] J.L. Shumaker, C. Crofcheck, S.A. Tackett, E. Santillan-Jimenez, M. Crocker, Catal. Lett. 115 (2007) 56.
[12] J.L. Shumaker, C. Crofcheck, S.A. Tackett, E. Santillan-Jimenez, T. Morgan, Y. Ji, M. Crocker, T.J. Toops, Appl. Catal. B: Environ. 82 (2008) 120.
[13] W.L. Xie, Z.Q. Yang, H. Chun, Ind. Eng. Chem. Res. 46 (2007) 7942.
[14] C.S. MacLeod, A.P. Harvey, A.F. Lee, K. Wilson, Chem. Eng. J. 135 (2008) 63.
[15] G.C. Maiti, M. Baerns, Appl. Catal. A: Gen. 127 (1995) 219.
[16] D.M. Alonso, R. Mariscal, R. Moreno-Tost, M.D.Z. Poves, M.L. Granados, Catal. Commun. 8 (2007) 2074.