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Evaluation of the activity and stability of alkali-doped metal oxide catalysts for application to an intensified method of biodiesel production

Claire S. MacLeod [a,*], Adam P. Harvey [a,1], Adam F. Lee [b], Karen Wilson [b]

[a] *School of Chemical Engineering and Advanced Materials, University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, UK*
[b] *Department of Chemistry, University of York, Heslington, York YO10 5DD, UK*

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Abstract

A series of alkali-doped metal oxide catalysts were prepared and evaluated for activity in the transesterification of rapeseed oil to biodiesel. Of those evaluated, $LiNO_3/CaO$, $NaNO_3/CaO$, KNO_3/CaO and $LiNO_3/MgO$ exhibited >90% conversion in a standard 3 h test. There was a clear correlation between base strength and activity. These catalysts appeared to be promising candidates to replace conventional homogeneous catalysts for biodiesel production as the reaction times are low enough to be practical in continuous processes and the preparations are neither prohibitively difficult nor costly. However, metal leaching from the catalyst was detected, and this resulted in some homogeneous activity. This would have to be resolved before these catalysts would be viable for large-scale biodiesel production facilities.

Keywords: Biodiesel; Renewable fuel; Transesterification; Heterogeneous catalysis; Process intensification

1. Introduction

Biodiesel is defined by the European Parliament in Directive 2003/30/EC as a 'methyl-ester produced from vegetable or animal oil, of diesel quality, to be used as biofuel'. Replacing petroleum-derived diesel fuel with biodiesel reduces life-cycle global-warming gas emissions by 45% [1]. In addition, tailpipe emissions of carbon monoxide, particulates and hydrocarbons are significantly reduced [2], improving air quality in urban areas. Biodiesel is also non-toxic, bio-degradable [3] and reduces reliance on oil imports [4]. For these reasons the European Union, and other legislatures, are promoting the substitution of biodiesel for petroleum-derived diesel via tax relief and mandatory targets.

Commercially, biodiesel is produced by transesterification of triglycerides, the main constituent of vegetable oil, with methanol in the presence of an alkaline liquid catalyst, usually sodium or potassium methoxide, in a stirred tank reactor. The main disadvantage of this method is the formation of soaps due to the reaction of the alkaline catalyst with free fatty acids, or due to the saponification of the triglycerides and biodiesel [5]. These reactions consume the catalyst and hinder phase separation of the biodiesel product from the glycerol side-product, which in practice results in reduced yields. A further disadvantage is that the glycerol by-product contains salts from the neutralization of the catalyst. This necessitates a more costly purification process, if a high-purity, saleable glycerol is to be produced [6]. These disadvantages could, however, be removed by use of a heterogeneous catalyst.

Intensification of biodiesel production by heterogenizing the reaction step would improve the economics of the process. This would reduce the final product cost and, therefore, market penetration of biodiesel would increase. Biodiesel production is a relatively immature industry, where new variations of plants are currently being designed and built, so improvements to the process can still be implemented. Also, heterogenization of the reaction step is a change that can be made to many existing plants retrospectively.

The use of a heterogeneous catalyst leaves no neutralization salts in the glycerol by-product, and, as the catalyst is not continuously added and disposed of, the inputs and waste are reduced. The catalyst can also be retained in the reactor by a simple filtration, and does not need to be neutralized to quench the reaction as in conventional technology, so the

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[*] Corresponding author. Tel.: +44 191 222 7268; fax: +44 191 222 5292.
E-mail addresses: c.s.macleod@ncl.ac.uk (C.S. MacLeod), a.p.harvey@ncl.ac.uk (A.P. Harvey).

[1] Tel.: +44 191 222 7268; fax: +44 191 222 5292.

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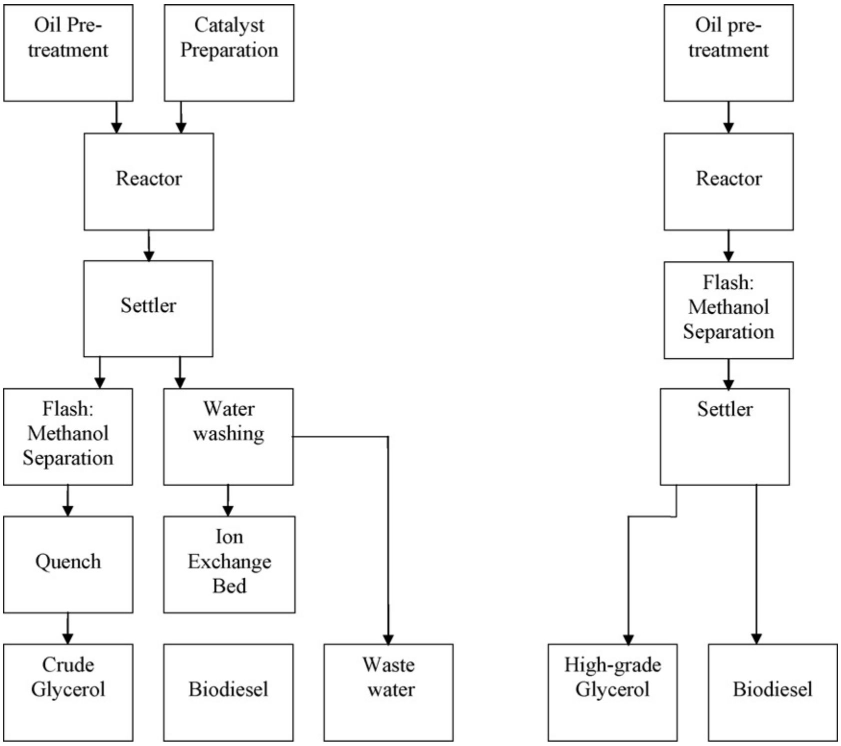

Fig. 1. Left: conventional flowsheet for biodiesel production; right: modified flowsheet for heterogeneously catalysed process.

number of separation steps downstream can be reduced, as shown in Fig. 1. The Esterfip-H process produces 160,000 t/year of biodiesel using a heterogeneous spinel-based catalyst, but operates at higher temperatures (~200 °C) than conventional processes [7]. The savings from the reduction in downstream separation stages must be more than equal to the extra cost of the higher temperature process. The promise of a cheaper process has resulted in a large body of research into heterogeneous catalysts for biodiesel [6,8–10]. Various catalysts have been evaluated with varying degrees of success, with solid bases generally observed to be more active than metal compounds [10]. Solid acids tend to require more extreme reaction conditions than solid bases [11]. Solid bases are the most studied class of catalysts. Most studies concluded activity increased with base strength and pore size.

Producing biodiesel is a bulk process, so any industrially practical catalyst must be easy to prepare on a large scale. For this reason alkali metal-doped metal oxides were studied, as the preparation method is relatively simple. Additionally, these types of catalysts have shown promising activities for transesterification reactions. Li impregnated CaO has been shown to give greater than 90% conversion after 10 min for the transesterification of tributyrate (a short chain triglyceride), where tributyrate was used as a model substrate for vegetable oil [9]. Alkali metal salts loaded on alumina also catalysed the transesterification of vegetable oil with methanol [8,12], and alkali metal salts on magnesium oxide showed some activity for the transesterification of vegetable oil [6].

In this work the effects of the alkali metal dopant (Li, Na, K), the support (CaO, MgO, Al_2O_3), and preparation method (calcined at 600 °C or heated to 110 °C) on the catalysts' activities were investigated. The reusability and thus also the degree of heterogeneity of these catalysts have also been studied. This information is vital for application to an industrial process. Once active catalysts were identified, then other reaction parameters (molar excess of methanol and amount of catalyst) were varied in order to define the reaction conditions necessary for a heterogeneously catalysed reaction to meet the European standards (EN14214) for biodiesel to be sold as a fuel.

2. Material and methods

2.1. Catalyst preparation

Catalysts were prepared by the incipient wetness method. Reagent grade CaO (Fisher), MgO (VWR) and γ-Al_2O_3 (Merck) were used as supports and reagent grade $LiNO_3$, $NaNO_3$ and KNO_3 (all Fisher) as the source of alkali metals. The alkali salts were dissolved in distilled water to give an alkali metal loading of 5 wt% on the support, the solution mixed with the support and the resulting paste dried in an oven at 110 °C for 5 h, and then calcined at 600 °C for 5 h, if required.

2.2. Characterization

Catalyst surface area was measured using the BET isotherm method in a Micromeritics Pulse Chemisorb 2700. Samples were degassed at 373 K under flowing argon, and then the adsorption of N_2 at 77 K was measured. The base strength was determined using Hammett indicators dissolved in methanol following the method of Watkins [9].

2.3. Catalyst screening

Food-grade rapeseed oil (Henry Colbeck) was used as the triglyceride source and reacted with reagent grade methanol (Fisher). As an initial test of activity, small-scale reactions were carried out in parallel: 0.2 g of catalyst was added to a 6:1 molar ratio of methanol to oil in a 2 ml sealed vial which was shaken in a IKA mini shaker at 600 rpm inside an incubator kept at 60 °C. After 3 h the reaction products were analysed by gas chromatography using the method of Plank and Lorbeer [13]. One hundred milligrams of the biodiesel sample was silylated with MSTFA, then internal standards of butane-1,2,4-triol and tricaprin were added. A Unicam Pro GC gas chromatograph was used with a J&W Scientific DB-1HT 15 m × 0.32 mm column.

2.4. Batch reactor test

Forty millilitres of methanol and 165 ml vegetable oil (6:1 molar ratio) were mixed with a magnetic stirrer in a 400 ml sealed glass jacketed vessel at 60 °C. A ~5 ml sample was taken periodically, filtered and then analysed by gas chromatography.

2.5. Reusability

The reaction mixture was analysed for alkali and alkaline earth metal content using flame photometry and atomic absorption spectroscopy. The activity of the dissolved metals was then tested by contacting the catalysts with methanol for 3 h at 60 °C, filtering to remove solids and then reacting vegetable oil with the catalyst leachate. The reaction product was then analysed by gas chromatography to assess the mass of biodiesel formed. 5 cycles of the reaction with the same catalyst were performed in the small scale shaker to assess if the conversion dropped after repeated use.

3. Results and discussion

3.1. Initial screening

The surface areas of the CaO supported catalysts (~10 m^2/g) and MgO supported catalysts (~20 m^2/g) were low while the Al_2O_3 supported catalysts had higher surface areas (~70 m^2/g). Calcining the CaO- and MgO-based catalysts significantly reduced the surface areas to 1–2 m^2/g. Compared to conventional catalysts, the surface areas are low, but there is no benefit in increasing surface area by increasing porosity. Triglycerides are large molecules and would be unable to diffuse into the pores, unless a mesoporous substrate was used.

The base strengths of the catalysts are shown in Table 1, measured using Hammett indicators. The alkali-metal doped CaO catalysts (calcined and uncalcined) show higher base strength than CaO alone ($8.2 < pK_{BH+} < 10.1$). This means doping the CaO with an alkali metal enhances the base strength of the catalyst, and calcination is not required to enhance the base strength. The increase in base strength on alkali promotion is thought to be due to the formation of O^- centres through the substitution of M^+ ions into the alkaline earth oxide lattice [14].

Table 1
Base strength of the tested catalysts and conversion achieved in initial screening (60 °C, 3 h, 6:1 molar ratio methanol to oil, 5% catalyst)

Catalyst	Base strength (pK_{BH+})	Conversion (%)
$LiNO_3/CaO$	$11 < pK_{BH+} < 15$	85
$NaNO_3/CaO$	$11 < pK_{BH+} < 15$	98
KNO_3/CaO	$11 < pK_{BH+} < 15$	90
$LiNO_3/CaO$ (calcined)	$11 < pK_{BH+} < 15$	99
$NaNO_3/CaO$ (calcined)	$11 < pK_{BH+} < 15$	100
KNO_3/CaO (calcined)	$11 < pK_{BH+} < 15$	100
$LiNO_3/MgO$	$8.2 < pK_{BH+} < 10.1$	5
$NaNO_3/MgO$	$10.1 < pK_{BH+} < 11$	4
KNO_3/MgO	$10.1 < pK_{BH+} < 11$	4
$LiNO_3/MgO$ (calcined)	$11 < pK_{BH+} < 15$	100
$NaNO_3/MgO$ (calcined)	$10.1 < pK_{BH+} < 11$	7
KNO_3/MgO (calcined)	$10.1 < pK_{BH+} < 11$	4
$LiNO_3/Al_2O_3$	<8.2	8
$NaNO_3/Al_2O_3$	<8.2	3
KNO_3/Al_2O_3	<8.2	6
$LiNO_3/Al_2O_3$ (calcined)	$10.1 < pK_{BH+} < 11$	5
$NaNO_3/Al_2O_3$ (calcined)	$10.1 < pK_{BH+} < 11$	6
KNO_3/Al_2O_3 (calcined)	$10.1 < pK_{BH+} < 11$	5

When MgO is used as a support, the base strength is lower. After calcination the base strength of Li on MgO increased, but there was no change after calcination for Na and K on MgO. The active centres on a Li doped MgO catalyst for the oxidative coupling of methane were identified as [Li^+O^-]. These centres could not be formed on Na doped MgO as the Na^+ ions are too large to substitute for Mg^{2+} ions [15]. Therefore active centres can be assumed only to form when Li is doped onto a MgO support. This size effect is not seen on CaO supports as the Ca^{2+} ion is larger.

None of the alumina supported catalysts achieved a high level of base strength, although, after calcination, the base strength of the alumina-supported catalysts increased. The origin of basicity on alumina support is thought to arise from the decomposition of salt anion (carbonate or nitrate) to form an O^- anion [16]. The base strength increased with coverage of alkali cation, and the most basic catalysts had 35 wt% K on alumina, which is much higher than the loading in this study [8]. Therefore only a moderate base strength was obtained.

Catalysts with enhanced base strength are active for the transesterification of vegetable oil: namely alkali-doped CaO catalysts and Li-doped MgO after calcination. After 3 h reaction, conversions in excess of 90% were achieved. Every catalyst with a base strength of higher than $pK_{BH+} > 11$ was active, showing that base strength is the most important factor. There is no significant effect in changing the alkali metal dopant on CaO supported catalysts. None of the alumina-supported catalysts are active, but the catalysts here have a lower loading of alkali metal (5%) than the 15–45% used in previous studies [8].

The homogeneous base-catalysed reaction proceeds via the formation of a methoxide ion, which attacks the carbonyl group on the triglyceride to create a tetrahedral intermediate to form the biodiesel ester and lose the glycerol backbone [17]. It is likely that the heterogeneous base-catalysed reaction will proceed via a similar route, so the base strength must be high in order

Table 2
Reuse of catalysts—comparison of triglyceride levels (mass %) after 1 cycle and 5 cycles of reaction

Catalyst	1st cycle	5th cycle
$LiNO_3/MgO$ (calcined)	1.4%	1.9%
$LiNO_3/CaO$	<0.1%	<0.1%
$LiNO_3/CaO$ (calcined)	0.3%	0.8%
$NaNO_3/CaO$	1.4%	0.2%
$NaNO_3/CaO$ (calcined)	<0.1%	0.5%
KNO_3/CaO	<0.1%	0.3%
KNO_3/CaO (calcined)	<0.1%	<0.1%

that a proton can be abstracted from the methanol to attack the carbonyl group. Other studies on solid catalysts have noted an improvement in activity with increasing base strength [10,18].

3.2. Reusability

Table 2 compares the conversion after 1 cycle and 5 cycles of reaction for each of the active catalysts. In general the conversions do not drop significantly after 5 cycles. This test shows that the reuse characteristics of these catalysts are good, however, their lifetime in an industrial setting would have to be significantly longer to be practical.

As the reaction is normally catalysed by homogeneous alkali metal hydroxides or methoxides, it is important to ensure that these species are not present due to leaching from the solid catalyst, and responsible for the observed activity of these solid catalysts. Table 3 shows the residual alkali metal concentration in the reaction mixture. The catalysts lose some alkali metal to the during the reaction. This amount of metal, although small, would still have to be removed in order for biodiesel to meet the standard EN14214. There was a loss of Ca into the reaction mixture, with concentrations of Ca in the region 200–600 ppm, the loss of Mg was much lower, resulting in concentrations in the reaction mixture of approximately 30 ppm.

If the dissolved metals are inactive then the catalysis is truly heterogeneous, but the loss of material over time will present problems. If, however, the dissolved metal is catalytically active then the catalysis is at least in part homogeneous, and the process advantages of the solid catalyst are lost. Table 4 shows the activity of the leachate, the activity of a methanol solution that was contacted with the catalyst for 3 h at 60 °C. All of the catalyst leachates tested showed at least some activity, so the catalysis is not entirely heterogeneous. Although testing the activity of the methanol leachate subjects the catalyst to more aggressive conditions than those experienced during the reaction, it would be expected that under reaction conditions at least some of the activity from these catalysts is due to homogeneous catalysis. Leaching from the catalyst will eventually reduce the activity of the catalyst, and the dissolved metals must be removed from the biodiesel before it is sold. Therefore, unless the stability of these catalysts can be improved significantly, none will be suitable for industrial use.

Table 3
Residual alkali metal levels in reaction mixture as measured by flame photometry and atomic absorption spectrometry

Catalyst	Tested metal	Concentration (ppm)
$LiNO_3/MgO$ (calcined)	Li	98
$LiNO_3/CaO$	Li	22
$LiNO_3/CaO$ (calcined)	Li	18
$NaNO_3/CaO$	Na	78
$NaNO_3/CaO$ (calcined)	Na	52
KNO_3/CaO	K	36
KNO_3/CaO (calcined)	K	32

Table 4
% mass biodiesel formed by reaction of oil with the catalyst leachate

Catalyst	% mass biodiesel formed
$LiNO_3/MgO$ (calcined)	26
$LiNO_3/CaO$	44
$LiNO_3/CaO$ (calcined)	54
$NaNO_3/CaO$	15
$NaNO_3/CaO$ (calcined)	29
KNO_3/CaO	3
KNO_3/CaO (calcined)	14

Reaction conditions were 3 h at 60 °C with a 6:1 molar ratio methanol to oil.

In general, these tests of reusability, in particular the leachate activity test, are not reported in much of the literature surrounding heterogeneous catalysts for biodiesel production. For a catalyst to be industrially useful, it must be stable.

3.3. Batch tests

Fig. 2 shows the reaction profiles with (a) CaO, (b) Li NO_3/CaO, (c) $NaNO_3/CaO$, (d) K NO_3/CaO, (e) KNO_3/CaO (calcined) and (f) $LiNO_3/MgO$ (calcined) catalysts. The conversion obtained after 180 min with CaO as a catalyst is poor, as expected, as it does not have a high base strength. However, 70% of the triglycerides are converted to lesser glycerides and biodiesel. This is attributed to the formation of calcium methoxide on the surface of CaO [19].

The reactions catalysed by $LiNO_3/CaO$, $NaNO_3/CaO$ and KNO_3/CaO exhibit similar conversions after 180 min, this shows that changing the alkali metal on the catalyst does not significantly affect activity. When the KNO_3/CaO was calcined the reaction rate increased. The possible structure change on calcination increases the activity of the catalyst. The $LiNO_3/MgO$ catalysed reaction exhibited the highest rate; less than 2% triglyceride remained after just 40 min.

The alkali-doped CaO catalysed reactions have similarly shaped conversion-time profiles: a high initial rate of reaction; then a plateau with a simultaneous increase in the concentration of mono- and di-glycerides; finally, after the plateau section the concentration of triglycerides decreases, with the concentration of partial glycerides decreasing more slowly. This plateau section was somewhat reduced when the KNO_3/CaO catalyst was calcined. However, the $LiNO_3/MgO$ catalyst did not exhibit the same profile; in fact the profile was more conventional, as the concentrations of partial glycerides peaked early on in the reaction and were consumed as the reaction progressed.

The conversion-time profile of the alkali-doped CaO catalysed reaction has a different shape to that of the homogeneously

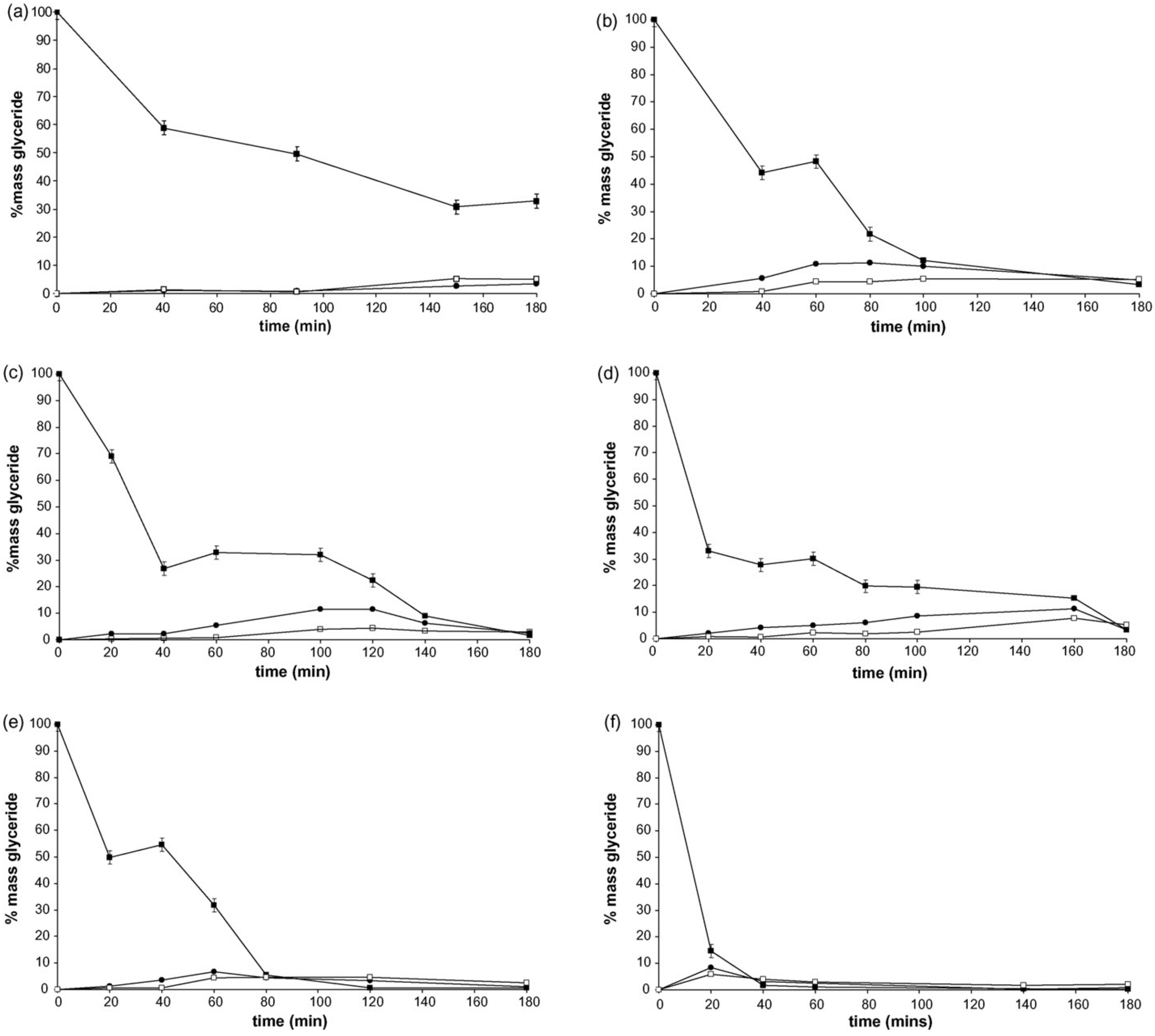

Fig. 2. (a) CaO catalysed reaction, 60 °C, 6:1 molar ratio oil to methanol, 2 g catalyst. Triglycerides ■, diglycerides ●, monoglycerides □. Error shown due to sampling errors, error in analysis too small to show. (b) $LiNO_3$/CaO catalysed reaction, 60 °C, 6:1 molar ratio oil to methanol, 2 g catalyst. Triglycerides ■, diglycerides ●, monoglycerides □. (c) $NaNO_3$/CaO catalysed reaction, 60 °C, 6:1 molar ratio oil to methanol, 2 g catalyst. Triglycerides ■, diglycerides ●, monoglycerides □. (d) KNO_3/CaO catalysed reaction, 60 °C, 6:1 molar ratio oil to methanol, 2 g catalyst. Triglycerides ■, diglycerides ●, monoglycerides □. (e) KNO_3/CaO calcined catalysed reaction, 60 °C, 6:1 molar ratio oil to methanol, 2 g catalyst. Triglycerides ■, diglycerides ●, monoglycerides □. (f) $LiNO_3$/MgO catalysed reaction, 60 °C, 6:1 molar ratio oil to methanol, 2 g catalyst. Triglycerides ■, diglycerides ●, monoglycerides □.

catalysed reaction, in which the partial glycerides exhibit a maximum concentration shortly after the start of the reaction. They are then consumed as the reaction progresses, and their concentration decreases to, and remains, close to zero [20]. Similarly in heterogeneously catalysed short-chain triglyceride transesterification reactions the concentrations of the partial glycerides peaked at the beginning of the reaction period [9,21]. The reaction between soybean oil and methanol at 100 °C catalysed by a zeolite also exhibited a peak in partial glyceride concentration at the start of the reaction [10]. Therefore it is unlikely that the plateau is a chemical effect, as we would expect the mechanism and reaction scheme to be essentially the same. It is more probable that the plateau region is due to a mass transfer limitation.

The transesterification of triglycerides to biodiesel consists of three sequential steps (Fig. 3). The triglyceride reacts with methanol to create a diglyceride, losing a fatty acid methyl ester (the "biodiesel"), then the diglyceride reacts with methanol to create a monoglyceride and a second fatty acid methyl ester. The monoglyceride then loses its final fatty acid chain as a fatty acid methyl ester to leave glycerol. Glycerol is a very viscous substance and could coat the catalyst particles, creating a mass

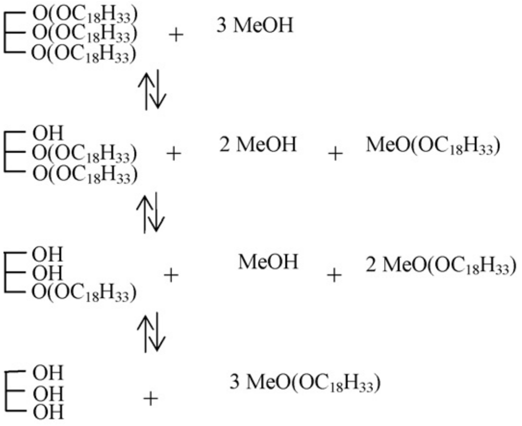

Fig. 3. Sequential transesterification of triglyceride with methanol to biodiesel (fatty acid methyl ester) and glycerol.

transfer film. The partial glycerides could also coat the catalyst particle. With reference to Fig. 2(b), (the $LiNO_3/CaO$ catalysed reaction), Fig. 2(c), (the $NaNO_3/CaO$ catalysed reaction) and Fig. 2(d), (the KNO_3/CaO catalysed reaction), it can be observed that the reaction rate slows dramatically after 40 min. At these times approximately 70% of the triglycerides have reacted to biodiesel and glycerol, and there are negligible concentrations of partial glycerides at this point. Glycerol is insoluble in biodiesel and forms a separate phase, and so will not be washed off the catalyst particle as the biodiesel is, and could create a film. The presence of this film could have two effects: firstly it could present a mass transfer barrier to the methanol and triglycerides and, secondly, it could create a local environment to the catalyst that is rich in glycerol and relatively poor in methanol and triglycerides, which would decrease the local conversion, pushing the equilibrium of the reaction (see Fig. 3) back towards the reactants, thereby favouring the formation of the intermediate products This proposed phenomenon leads to the two effects seen on the reaction profiles: the plateau, and the relatively high concentration of partial glycerides.

The percentage mass of the glycerides remaining for each catalyst is shown in Table 5. By comparing the remaining glycerides with the level set by EU standard EN14214 (also shown in Table 5) it can be seen that the biodiesel produced does not meet the standard and would have to be purified before being sold. The $LiNO_3/MgO$ catalysed reaction meets the standard set for triglyceride level, but not for mono- and di-glyceride levels.

To reduce costs, the amount of purification required should be minimised, and the conversion should be as close as possible to 100% to reduce the number of purification steps and the duties upon them. To achieve this, and to attempt to meet the EU standard, a number of reaction conditions were varied for KNO_3/CaO to investigate the extent to which the conversion could be increased. The remaining glycerides after 1, 2 and 3 h are shown in Table 6. Increasing the amount of catalyst added from 2 to 4 g did not increase the rate of the reaction, as, after 60 min 20% mass triglyceride remained, which is comparable to the reference reaction. The final concentrations of mono-, di- and triglycerides were reduced from the reference levels though. Increasing the molar ratio of methanol increased the rate of the reaction, such that only 5% mass triglyceride remained after 1 h, and the final concentrations of glycerides were also slightly reduced. However, neither method brought the biodiesel produced in line with the standard. It appears that the challenge in heterogenizing the reaction step in biodiesel production is achieving >99% conversion. As the reaction approaches completion, the remaining glycerides must contact the catalyst and methanol to react to biodiesel. The better mixing of a homogenous catalyst makes this more likely and so a higher conversion would be reached after 3 h.

As the formation of a glycerol film slows the reaction by creating a mass transfer barrier, a two-stage process was also tested in which the products were removed from the reactor after 30 min, the liquid separated from the catalyst and returned to the reactor with the addition of new catalyst. A comparison of the glyceride concentrations in the one and two stage processes is shown in Table 7 and Fig. 4. The biggest difference is that after 40 min in the two-stage process there is only 6% mass triglyceride, but in the one-stage process there is 54% mass triglyceride. There does appear to be a clear advantage in the two-stage process, as fresh catalyst without a film of glycerol allows the reaction to proceed unhindered. This result offers some evidence that there is a mass transfer limitation. This is not simply deactivation of the

Table 5
Remaining glycerides after 180 min reaction, compared to EU standard

Catalyst	Monoglyceride (% mass)	Diglyceride (% mass)	Triglyceride (% mass)
$LiNO_3/CaO$	5.2	5.0	3.3
$NaNO_3/CaO$	2.9	2.5	1.6
KNO_3/CaO	5.3	3.2	3.4
KNO_3/CaO (calcined)	2.5	1.1	0.7
$LiNO_3/MgO$ (calcined)	2.2	0.9	0.1
EU standard EN14214	0.8	0.2	0.2

Table 6
Remaining glycerides with 4 g KNO_3/CaO calcined catalyst (2× increase) and 9:1 molar ratio methanol to oil (1.5× increase) at 1, 2 and 3 h

Time (h)	4 g KNO_3/CaO calcined catalyst			9:1 molar ratio methanol to oil		
	Monoglyceride (% mass)	Diglyceride (% mass)	Triglyceride (% mass)	Monoglyceride (% mass)	Diglyceride (% mass)	Triglyceride (% mass)
1	2.2	9.0	20.2	3.1	0.4	4.9
2	1.7	1.2	1.6	4.1	0.2	1.0
3	1.5	0.5	0.4	2.4	1.1	0.3

Table 7
Comparison of 1- and 2-stage processes

Time (min)	One stage			Two stage		
	Monoglycerides (% mass)	Diglycerides (% mass)	Triglycerides (% mass)	Monoglycerides (% mass)	Diglycerides (% mass)	Triglycerides (% mass)
20	0.7	1.2	50.0	0.7	1.2	50.0
40	0.6	3.6	54.0	6.7	7.6	5.7
80	4.7	4.5	5.5	3.1	2.3	1.1

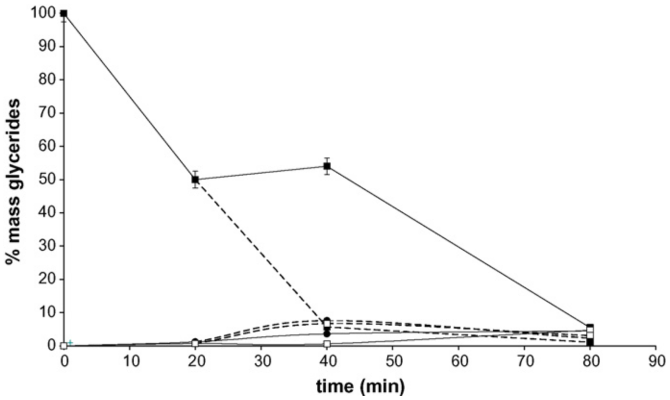

Fig. 4. KNO$_3$/CaO (calcined) catalysed two stage reaction, fresh catalyst added after 30 min, 60 °C, 6:1 molar ratio oil to methanol, 2 g catalyst. Triglycerides ■, diglycerides ●, monoglycerides □. One stage process solid lines, two stage process dotted lines.

catalyst, as the catalyst has been demonstrated to be reusable for a short time. The advantage of the two-stage process decreases at longer times, and after 80 min the glyceride concentration in the two-stage process is only slightly less than for the one stage process. So in the two-stage process the plateau region is removed, but the reaction does not proceed fully to completion because it is limited by the equilibrium between glycerol and partial glycerides.

4. Conclusions

Four active catalysts for the transesterification of rapeseed oil to biodiesel have been identified: LiNO$_3$/CaO, NaNO$_3$/CaO, KNO$_3$/CaO and LiNO$_3$/MgO (only after calcination). These catalysts are novel for this application. There is a clear correlation between their base strength and their catalytic activity. The time for the reaction to progress to a reasonable conversion is not prohibitively long, especially in the case of LiNO$_3$/MgO, the most active catalyst, where after 40 min less that 5% triglycerides remain.

Reusability has been demonstrated for these catalysts, although it has also been demonstrated that there is some degree of catalyst leaching, and this leaching creates some homogeneous catalytic activity. This would need to be minimised for the catalysts to have a reasonable lifetime in an industrial setting. There is also some degree of mass transfer limitation, possibly caused by the formation of a glycerol film limiting access to the active sites of the catalyst. This can be partially overcome by employing a two-stage process.

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