

Tunable and efficient catalysts for the simultaneous trans-esterification of lipids and esterification of free fatty acids from bio-oil for an effective production of FAMES

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Introduction

The utilization of aquatic biomass as source of biodiesel will rise the problem of conversion of bio-oil into a fuel that meets the EU (or international) specifications. Bio-oil as extracted from macro- or micro- algae cannot be used in existing engines for several reasons, among which: i) it is a derivative of glycerol (Triglycerides-TG, Diglycerides-DG, Monoglycerides-MG) and its viscosity does not make it suited for a direct use; ii) it may contain up to 20% free fatty acids-FFAs; iii) it is formed by a mixture of poly-unsaturated fatty acids-PuFAs. An approach to the treatment of bio-oil is necessary that may master all the issues above. In this paper we describe our approach to solving the problem of the simultaneous trans-esterification of lipids (that require a basic catalyst) and esterification of FFAs (that require an acid catalyst), using new mixed oxides properly prepared. New mixed oxides based on calcium, cerium and aluminium have been used as catalysts in the trans-esterification of extra virgin oil as a test case. The same catalysts have been used in the simultaneous direct trans-esterification of lipids and esterification of FFAs present in a natural matrix such as lampante olive oil. Finally, the catalysts have been used in the production of biodiesel from non edible oil, such as that extracted from aquatic biomass (*Nannochloropsis sp microalgae*).

Experimental

The lipids have been extracted from dry and grinded *Nannochloropsis sp. microalgae*, using different systems as reported in Table 1

Table 1: Amount of biooil and FAMES obtained under different conditions from *Nannochloropsis sp.*

Extraction Method	Biomass dry weight (g)	Working Conditions		Lipid extraction solvent (mL)	Yield bio-oil (%)	Yield FAMES (%)
		Temp (K)	Time (min)			
Soxhlet	5	> 343	360	<i>n</i> -Hexane (50)	9	8
				Chloroform:methanol 1:2 (50)	40	24
US assisted	1.20	293	60	<i>n</i> -Hexane (33)	3.3	8.3
	1.58	323			3.6	8.9
	1.87	343			4.0	7.8
	1.29	293		Chloroform:methanol 1:2 (50)	40	35
	1.76	323			38	33
	2.06	343			39	34
Thermochemical liquefaction	20	523	60	CH ₂ Cl ₂ (3 x 5 mL)	68	8

The preparation of mixed oxides based on Al/Ca/Ce was made using a solid state synthesis. The solid obtained by High Energy Milling (HEM) was calcined for 3 h at the temperature of 823 K or at 1373 K to obtain the final oxides that have been characterized through elemental analysis, BET, TPD and XPS.

For the study of the reactivity of catalysts in the trans-esterification reaction, 1.8 g of oil in a steel autoclave was reacted with 5 mL of methanol (molar ratio methanol:oil 50:1) at 453 K and 5.0 MPa of N₂ for 3 h. In each test 50 mg of catalyst were used (2.8 % w catalyst/w oil).

The one-pot "CATEXTR" technology for the direct catalytic extraction of FAMES from microalgae using either 12CaO·7Al₂O₃·7CeO₂ or CeO₂/CaO is described in the Italian Patent to ENI H10008, 2010.[1]

The quantification of FAMES was performed according to the regulations (CE) n. 796/2002.

Results and Discussion

The activity of the newly synthesized nanocatalysts was determined by trans-esterification of extra-virgin olive oil. From obtained data (Table 2) it is clear that catalysts calcinated at 823 K are more active in the trans-esterification of extra virgin olive oil than those calcinated at 1373 K, probably because of the negative effect of the reduction of the active surface at higher temperature.

We have focused our attention on the activity and the resistance of the mixed oxides calcined at 823 K, because the separation of the catalyst is very easy and efficient. In detail we have tested the 12CaO·7Al₂O₃·7CeO₂ stability in recycling tests with fresh oil and methanol because this catalyst results to be more stable than CaO-CeO₂. The obtained results show a very good stability of the catalyst without any loss of activity also after five cycles of reaction.

Table 2 : Trans-esterification of extra-virgin oil using several mixed oxides.

Entry	T (K)	Catalysts	% Composition of the organic phase				Saponifiable matter
			FAMEs	MG	DG	TG	
1	823	CaCO ₃	7.6	1.55	8.20	72.37	89.72
2		Al ₂ O ₃	15.1	3.69	8.66	62.93	90.38
3		CeO ₂	11.1	0.90	6.00	75.63	93.63
4		CaO CeO ₂	97.0	0.79	0.07	0.11	97.97
5		12 CaO 7Al ₂ O ₃	50.4	11.16	8.75	20.17	90.48
6		12 CeO ₂ 7Al ₂ O ₃	5.7	0.31	3.71	84.56	94.28
7		12 CaO 7Al ₂ O ₃ 3 CeO ₂	96.8	0.83	0.02	0.05	97.70
8		12 CaO 7Al ₂ O ₃ 7 CeO ₂	96.7	0.65	0.01	0.01	97.37
9		12 CaO 7Al ₂ O ₃ 12 CeO ₂	97.1	0.81	0.01	0.01	97.93
10	1373	CaCO ₃	97.5	0.91	0.01	0.01	98.43
11		Al ₂ O ₃	10.2	2.25	8.58	68.74	89.77
12		CeO ₂	3.1	0.35	4.69	83.01	91.15
13		12 CaO 7Al ₂ O ₃	96.5	0.79	0.01	0.09	97.39
14		12 CaO 7Al ₂ O ₃ 3 CeO ₂	34.1	9.78	12.14	34.16	90.18
15		12 CaO 7Al ₂ O ₃ 7 CeO ₂	92.0	1.07	0.01	0.02	93.10
16		12 CaO 7Al ₂ O ₃ 12 CeO ₂	64.0	8.45	4.85	8.33	85.63

In Table 3, we report the experimental results of the direct conversion of a lampante olive oil into FAMES: it is of interest to compare the activity of quaternary, ternary and binary metal oxide systems. Mixed oxides Ca/Ce show good activity in transesterification and in the direct esterification of FFAs, better than that of catalytic systems constituted from Al/Ce and Ca/Al.

Table 3: Reactivity of various mixed oxides in the trans-esterification of lampante oil.

Entry	Catalysts	% Composition of the organic phase					Saponifiable matter
		FAMEs	MG	DG	TG	FFA	
1	CaCO ₃ calcinated at 823 K	17.92	3.85	13.52	47.17	14.57	97.03
2	CaCO ₃ calcinated at 1373 K	73.80	3.85	2.22	0.54	17.00	97.41
3	Al ₂ O ₃	13.22	2.61	11.96	54.88	15.70	98.37
4	CeO ₂	26.49	0.55	7.67	63.23	0.32	98.26
5	0.1 CaO CeO ₂	33.15	3.59	11.76	46.36	0.78	95.64
6	0.5 CaO CeO ₂	47.78	3.61	10.21	34.80	0.80	97.20
7	CaO CeO ₂	95.62	0.91	0.02	0	0.68	97.23
8	Al(3%) CeO ₂	32.25	2.51	13.12	49.4	0.82	98.10
9	CaO Al ₂ O ₃	28.57	5.85	13.98	35.97	13.45	97.82
10	12 CaO 7Al ₂ O ₃	33.76	7.16	11.02	26.80	17.5	96.24
11	12 CaO 7Al ₂ O ₃ 7 CeO ₂	95.48	0.88	0.01	0.01	0.70	97.08

As it is shown in Table 1 the US assisted extraction using the binary mixture of solvents (C:M) is the most effective extraction system as evident from the amount of biooil and biodiesel obtained. We have used several catalysts of different composition CaO:CeO₂ in order to check their ability in the simultaneous trans-esterification of lipids and esterification of FFAs. Table 4 clearly shows that catalysts more rich in acid sites (CeO₂) preferentially convert FFAs than lipids. Noteworthy, increasing the content of CaO into the mixed oxide (from CeO₂ to 0.1CaO/CeO₂, 0.5 CaO/CeO₂, CaO/CeO₂) the catalyst undergoes an increase of the number of basic sites and better converts the lipids, while maintaining a good conversion of FFAs.

Table 4: Conversion of lipids and FFAs with different catalysts (1 h reaction at 80 °C)

Catalysts	% Composition of organic phase				
	FAMEs	Monoglycerides	Diglycerides	Triglycerides	FFA
Oil used	0.0	3.7	8.8	69.9	16.2
CaO CeO ₂	96.2	1.5	0.1	0.1	0.9
0.5 CaO CeO ₂	43.5	4.8	12.2	35.5	1.2
0.1 CaO CeO ₂	30.2	5.1	13.5	46.8	1.2
CeO ₂	23.1	2.2	8.8	63.6	0.6

Conclusions

We have investigated routes that may reduce the energetic and material costs in the production of biofuels applying processes for the simultaneous trans-esterification of lipids and esterification of FFAs using new mixed-oxides catalysts. Catalysts 12CaO·7Al₂O₃·7CeO₂ and CaO·CeO₂ show quite good properties for the simultaneous transesterification of lipids and esterification of FFAs [2].

References

1. M. Aresta, A. Dibenedetto, M. Ricci ENI patent H10008, 2010.
2. A. Dibenedetto, C. Pastore, L. di Bitonto, A. Colucci and M. Aresta *Energy and environmental Science submitted*

