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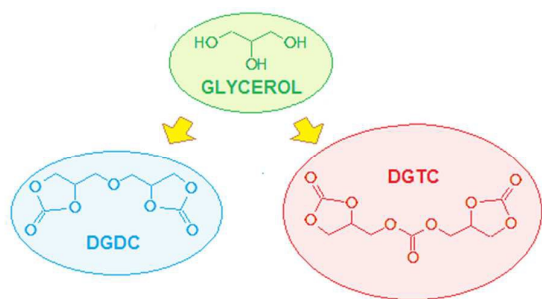
Mixed oxides have been used for the conversion of glycerol into DGDC and DGTC using either DMC or urea.

Journal Name

ARTICLE

New efficient and recyclable catalysts for the synthesis of di- and tri-glycerol carbonates

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Multifunctional monomers based on glycerol carbonate are employed in the chemical industry for the production of polyurethanes and polycarbonates. To avoid the use of toxic phosgene as carboxylating reagent, eco-friendly routes have been developed using alternative agents. In this paper, a series of binary and ternary oxides have been tested as catalysts in the synthesis of diglycerolether dicarbonate (DGDC) and diglycerol tricarbonate (DGTC) using dimethyl carbonate (DMC) and urea as carboxylating agents. The recovery and reuse of the catalysts are discussed. In the best reaction conditions, using mixed oxides La:Ca = 1:1 as catalysts, the yields of DGDC and DGTC were >90 (pure isolated compounds) and 19.9%, respectively.

1. Introduction

Over the last decade, glycerol production has considerably grown following the development of bio-oil industry for the production of biofuels and bio-lubricants.[1-7] In oleo-chemistry processes glycerol represents 10% of biodiesel, so that the growing demand of biodiesel is generating in some areas a significant excess of glycerol.[8-10] In addition, glycerol can be produced by enzymatic fermentation or catalytic hydrogenolysis of cellulose.[11-13] There is an industrial interest to find innovative uses of glycerol: both molecular compounds and polymers are an attracting perspective (Fig. 1).

Acrolein, obtained from the dehydration of glycerol,[14-19] is used in situ for the synthesis of acrylic acid.[20,21] The catalytic hydrogenolysis of glycerol is a route to increase the profitability of biodiesel production plants.[22-27] Products such us propylene glycols are used for the synthesis of polyester resins, liquid detergents, drugs and cosmetics.[28-32] Glycerol can also be converted into branched oxygen-containing components by catalytic etherification with alcohols or alkenes.[33-37] It can be dehydrated to glycidol[38,39] and used for the production of 1,3-propanediol *via* biotechnology.[40,41] The production of 3-hydroxypropanoic acid (3-HPA)[42,43] is also of interest as the latter can be used as monomer for polymers. Diglycerol ether is used for the production of polyesters[44,45] and cosmetics.[46] Glycerol carbonate is an interesting compound for the chemical industry. It is used as a component of polyurethane foams, gas separation membranes, surfactants, paints, detergents and as a non-volatile reactive solvent for several types of materials.[47-52] Due to its low toxicity, vapor pressure and
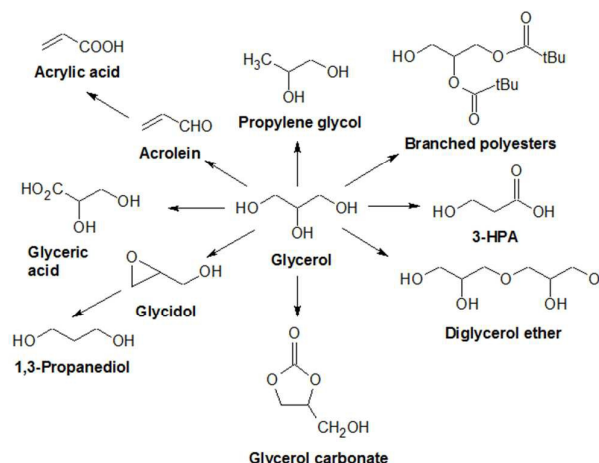

Fig. 1 Glycerol as a building block for the synthesis of chemicals.

flammability, good biodegradability and moisturizing ability, glycerol carbonate also possesses the right characteristics of a wetting agent for cosmetic clays or of a carrier for drugs[53,54] Glycerol carbonate is usually prepared by reacting glycerol with toxic phosgene:[55,56] innovative processes such as the direct carboxylation of glycerol with carbon dioxide,[47,57-59] the glycerolysis of urea[60-62] or the trans-esterification reaction with linear or cyclic organic carbonates[63-66] represent ecofriendly alternatives.
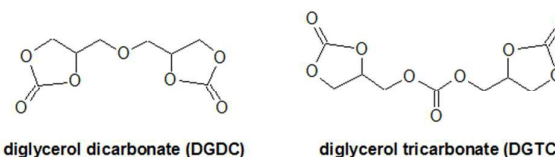

Fig. 2 Multifunctional monomers based on glycerol carbonate.

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In recent years, multifunctional monomers based on glycerol carbonate have reached a particular importance in the chemical industry for the production of polyurethanes and polycarbonates (Fig. 2).[67-71] Only a few methods are reported in the literature for the synthesis of such molecules. The trans-esterification of diglycerol ether for the synthesis of DGDC is a two-step process affording first 4-[(2,3 di-hydroxy-propoxy)methyl]-1,3 dioxolan-2-one, followed by the conversion of the latter into DGDC by further trans-esterification (Scheme 1).
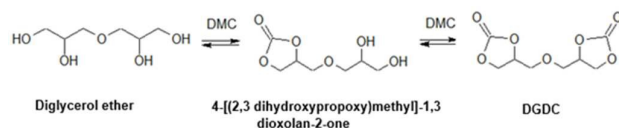
Scheme 1. Schematic presentation of the products obtained from the trans-esterification of diglycerol ether with DMC for the synthesis of DGDC.

Mignani et al.[72] have used lanthanum oxide as catalyst in the synthesis of diglycerol dicarbonate (DGDC) from diglycerol ether and DMC. The reaction was carried out at 393 K for 48 h and the final product was crystallized from methanol with an isolated yield of 90% with respect to diglycerol ether, but neither DGDC was fully characterized nor the catalyst was recovered and reused.

Weckhuysen et al.[73,74] have studied hydrotalcites Mg:Al in the same trans-esterification process. Using hydrotalcite Mg:Al = 5 molar ratio a yield of 86% of DGDC with a selectivity of 89% were obtained after 6h of reaction (T = 403 K). The catalyst was easily recovered and reused, but the production of the cyclic carbonate decreased after the first cycle of reaction. The quantification of the products obtained from the trans-esterification reaction was made using NMR, and DGDC was not isolated. Diglycerol tricarbonate (DGTC) is reported to be obtained from the trans-esterification reaction of glycerol with DMC using potassium carbonate.[71] A yield of 18% was reported after 48 h of reaction (T = 343 K), but the catalyst was not recoverable at the end of the reaction cycle.

In this paper, a series of binary and ternary oxides based on lanthanum have been synthesized and used as catalysts in eco-friendly routes for the synthesis of DGDC and DGTC. They were recovered and recycled. The various oxides are characterized by a different electronic configuration of the metal and acid/basic properties that can be tuned with the reaction they have to catalyze. In our study, we have set a relationship between catalyst composition and their properties such as: acid/basic sites, activity, recoverability and selectivity. Both dimethyl carbonate and urea have been used as reagents for building the carbonate moiety.

2. Experimental section

2.1 Materials and methods

All solvent and starting reagents were RP Aldrich products. Single metal oxides were previously calcined for 3 h at 823 K, to remove traces of moisture present. FTIR spectra were recorded with a Shimadzu Prestige 21 instrument. Mixed oxides were synthesized in the solid state by using High Energy Milling (HEM) technique with a Pulverisette 7 apparatus. Acid/basic sites were determined using a Micromeritics Chemisorb 2750 equipment. The analyses of the acid and basic sites were carried out using NH_3 and CO_2, respectively, as probe-gas with 100 mg of catalyst. The samples were pre-treated under N_2 flow (30 mL min^{-1}) at 823 K. The Pulse Chemisorb was performed using He as carrier gas (30 mL min^{-1}). The TPD were

performed under He flow at 30 mL min^{-1}. GC-MS analyses were carried out with a Shimadzu 17 A gas chromatograph (capillary column: 30 m; MDN-5s, Ø 0.25 mm, 0.25 μm film) coupled to a Shimadzu QP5050 A mass spectrometer. Quantitative determinations on the reaction solution were performed using a Hewlett Packard 6850 GC-FID (capillary column: 30 m; Carbowax; Ø 0.25 mm, 0.25 μm film). The ^{1}H NMR and ^{13}C NMR spectra were recorded using a BRUKER 600 MHz. The synthesis and isolation of methyl-glyceryl-carbonate (MGC) was made as reported in literature.[71]

2.2 Catalysts preparation
2.2.1 Synthesis of mixed oxides

The synthesis of the mixed oxides La:Ca and La:Zn was carried out using a solid state method.[65,75] Depending on the expected composition of mixed oxides (Table 1) weighted amounts of lanthanum, calcium and zinc oxide were mixed in High Energy Milling-HEM apparatus (spheres and basket made of agata), for 1 h at 700 rpm. Then the resulting solid was calcined at 823 K for 3 h. To check the stability of the catalyst, the CaO-La$_2$O$_3$ mixed oxide was analysed after 10 runs and the Ca content was found to be 10.3% with respect to the theoretical value 10.5% in the starting material. The BET and Basic/Acid ratio were also practically unchanged with respect to the original catalyst.

2.2.2 Hydrotalcite Mg:Al = 5

Hydrotalcite Mg:Al = 5 was synthesized using a co-precipitation method.[74] 8.55 g of Na$_2$CO$_3$*10 H$_2$O and 2.80 g of NaOH were dissolved into 60 mL of deionized water. A solution containing 12.82 g of Mg(NO$_3$)$_2$·6H$_2$O and 3.75 g of Al(NO$_3$)$_3$·9H$_2$O (molar ratio = 5 : 1) into 100 mL of deionized water was then added dropwise. The mixture was stirred for 22 h at 373 K. Then, the white precipitate was filtered and washed (3 x 100 mL) with deionized water.
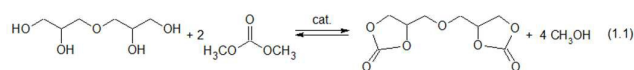
2.3 Diglycerolether dicarbonate

2.3.1 Trans-esterification of diglycerol ether with DMC

The trans-esterification reaction (Eq. 1.1) was carried out in a glass tube under atmospheric pressure of nitrogen. In each test 0.1 g of catalyst were used with 0.5 g of diglycerol ether (weight ratio catalyst: diglycerol ether = 20%) and 5.2 mL of DMC (ρ = 1.069 g mL^{-1}, molar ratio of DMC:diglycerol ether = 20:1). The system was heated under stirring at 355 K for 48 h using an oil bath. At the end of the reaction, the catalyst was recovered by centrifugation, washed with methanol and calcined for 3 h at 773 K. The products obtained (DGDC and 4-[(2,3 dihydroxypropoxy)methyl]-1,3 dioxolan-2-one), were dissolved into DMSO and analyzed by GC and GC-MS using diphenyl ether as standard.

Table 1. Amount of the reagents used for the synthesis of mixed oxides.

Catalysts			Reagents (g)		
			La$_2$O$_3$	CaO	ZnO
1		0.1	0.34	1.16	-
2	La:Ca	0.5	0.89	0.61	-
3		1	1.12	0.38	-
4		0.1	0.25	-	1.25
5	La:Zn	0.5	0.75	-	0.75
6		1	1.01	-	0.51

(1.1)

2.3.1.1 Isolation and characterization of diglycerolether dicarbonate

The crude product obtained as reported in 2.3.1 was evaporated in vacuum to eliminate excess DMC and the formed methanol that were condensed and recovered. The resulting liquid was kept at 278 K for 48 h to afford a white solid (>90%) that was separated from the residual liquid by filtration, washed with methanol (3 x 2 mL) and dried in vacuo.

Elemental analysis: calculated for $C_8H_{10}O_7$: % C calc 44.0, found:43.3; % H calc 4.58, found: 4.55.

Diglycerolether dicarbonate: ^{1}H NMR (600 MHz, DMSO-d[6]) δ = 4.93(m, 2H) OCH₂C*H*CH₂O, 4.52 (t, 2H) and 4.24 (q, 2H) OC*H₂*CHCH*H₂*O, 3.72(m, 4H) OCH₂CHC*H₂*O ppm.^{13}C NMR (600 MHz, DMSO-d[6]) δ = 66.21 O*C*H₂CHCH₂O, 70.65 and 70.68 OCH₂CH*C*H₂O, 76.11 and 76.21 OCH₂*C*HCH₂O, 155.10 and 155.12 (*C*(O)OO) ppm.
FTIR (KBr): 3000-2900 cm^{-1} (s, *C-H* stretch), 1790 cm^{-1} (s, *C=O* stretch), 1100 cm^{-1} (s, *C–O–C* stretch), 1401 (s, *CH₂* bend), 1176 cm^{-1} (s. *CH* bend).

2.3.2 Alcoholysis of urea with diglycerol ether

3 g of diglycerol ether, 2.16 g of powdered urea (molar ratio urea : diglycerol ether = 2 : 1) and 0.6 g of catalyst (weight ratio catalyst : diglycerol ether = 20%) were placed into the reactor connected to a vacuum system (20 Pa) to remove ammonia during the reaction (Eq. 1.2).[54,75] The mixture was heated under stirring at 423 K for 15 h. At the end of the reaction, the catalyst was recovered by centrifugation, washed with methanol and calcined for 3 h at 773 K. The products, DGDC and 4-[(2,3-di-hydroxy-propoxy)methyl]-1,3-dioxolan-2-one(DHPMC), obtained, were dissolved into DMSO and analyzed by GC and GC-MS using diphenyl ether as standard. The pure solid (90% yield) was isolated following the procedure described in 2.3.1.1.

2.4 Diglycerol tricarbonate

2.4.1 Trans-esterification of glycerol carbonate with DMC

3.27 g of glycerol carbonate, 480 µL of DMC (ρ = 1.069 g mL^{-1}, molar ratio glycerol carbonate:DMC=5:1) and 0.1 g of catalyst (weight ratio catalyst:DMC=20%), were placed into a glass tube under atmospheric pressure of nitrogen. The reaction was carried out at 413 K for 24 h (Eqs. 1.3-1.4). At the end of the reaction, the catalyst was recovered by centrifugation, washed with methanol and calcined for 3 h at 773 K and eventually reused. The obtained mixture (containing methyl-glyceryl-carbonate MGC and diglycerol tricarbonate DGTC), were dissolved into DMSO and analyzed by GC and GC-MS using benzophenone as standard. The yields of MGC and DGTC were 42.7 and 15.4%, respectively, with a selectivity of 73.5 and 26.5%.

Diglycerol tricarbonate: ^{1}H NMR (600 MHz, DMSO-d[6]) δ = 5.14(m, 2H) OCH₂C*H*CH₂O, 4.56 (t, 2H) and 4.36 (q, 2H) OC*H₂*CHCH₂O, 4.26 (m, 4H) OCH₂CHC*H₂*O ppm. ^{13}C NMR (600 MHz, DMSO-d[6]) δ = 65.89 O*C*H₂CHCH₂O, 67.27 and 67.32 OCH₂CH*C*H₂O, 74.53 and 74.56 OCH₂*C*HCH₂O, 155.49 and 155.51 (*C*(O)OO) ppm.

Methyl-glyceryl-carbonate: ^{1}H NMR (600 MHz, DMSO-d[6]) δ = 5.01(m, 2H) OCH₂C*H*CH₂O, 4.40 (t, 2H) and 4.30 (q, 2H) OC*H₂*CHCH*H₂*O, 4.10 (m, 4H) OCH₂CHC*H₂*O ppm, 3.72 (s, OCH₃). ^{13}C NMR (600 MHz, DMSO-d[6]) δ = 65.43 O*C*H₂CHCH₂O, 67.01 and 66.98 OCH₂CH*C*H₂O, 74.19 and 74.23 OCH₂*C*HCH₂O, 154.90 and 154.94 (*C*(O)OO) ppm.

(1.2)

(1.3)

(1.4)

(1.5)

(1.6)
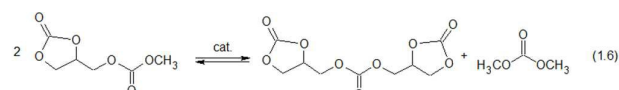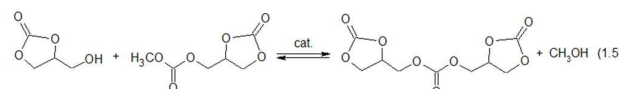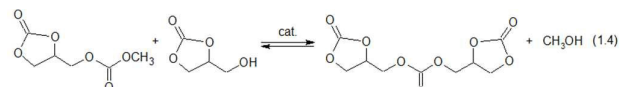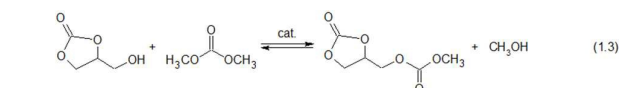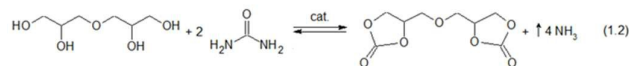
2.4.2 Trans-esterification of MGC with glycerol carbonate

0.25 g of MGC, 0.08 g of glycerol carbonate (molar ratio MGC : glycerol carbonate = 2 : 1)) and 0.05 g of catalyst (weight ratio catalyst : MGC = 20%) were placed into a glass tube under atmospheric pressure of nitrogen. The reaction was carried out at 413 K for 24 h (Eq. 1.5). At the end of the reaction, the catalyst was recovered by centrifugation, washed with methanol and calcined for 3 h at 773 K. The product obtained (DGTC), was dissolved into DMSO and analyzed by GC and GC-MS using benzophenone as standard. The yield of DGTC was 19.9% with a selectivity of 23%.

2.4.3 Disproportionation of MGC

0.25 g of MGC and 0.05 g of catalyst (weight ratio catalyst : MGC = 20%) were placed into a glass tube under atmospheric pressure of nitrogen. The reaction was carried out at 413 K for 24 h (Eq. 1.6). At the end of the reaction, the catalyst was recovered by centrifugation, washed with methanol and calcined for 3 h at 773 K. The products obtained (DGTC and DMC) were dissolved into DMSO and analyzed using benzophenone as standard. The yield of DGTC was 21.2% with a selectivity of 100% towards disproportionation.

3. Results and discussion

3.1 Diglycerol dicarbonate

3.1.1 Study of the catalytic activity of single metal oxides in the trans-esterification reaction of diglycerol ether with DMC

Table 2 shows the conversion, yield and selectivity of single metal oxides in the trans-esterification of diglycerol ether with DMC for the synthesis of DGDC (Eq. 1.1). The reaction conditions are recalled in the Table for reader convenience.

Table 2. Comparison of the catalytic activity of single metal oxides in the trans-esterification of diglycerol ether with DMC for the synthesis of DGDC.

	Catal.	% Conv. Diglycerol ether	% DHPMC		% DGDC		%w/w Recovery of the catalysts*
			Yield	Selectivity	Yield	Selectivity	
1	CaO	87.5	14.2	16.2	73.3	83.8	64.2
2	La$_2$O$_3$	70.4	32.0	45.4	38.4	54.6	98.5
3	MgO	69.6	33.2	47.7	36.4	52.3	82.3
4	PdO	40.4	37.8	93.6	2.6	6.4	96.4
5	SnO	35.9	33.5	93.3	2.4	6.7	98.1
6	Fe$_2$O$_3$	35.6	35.6	100	0	0	97.8
7	CeO$_2$	26.4	26.4	100	0	0	98.4
8	TiO$_2$	25.2	25.2	100	0	0	98.9
9	ZrO$_2$	24.3	24.3	100	0	0	98.6
	No catal.	12.4	12.4	100	0	0	-

Reaction conditions: molar ratio DMC:diglycerol ether=20:1, weight ratio catalyst:diglycerol ether = 20%, T=355 K, t=48 h. *At the end of the reaction, the catalyst was recovered and calcined for 3 h at 773 K.

Calcium oxide shows the best activity in the production of DGDC with a conversion of 87.5% with a yield of 73.3% and a selectivity of 83.8% towards DGDC (Table 2, Entry 1). However, the recovery of the catalyst results to be difficult due to the dissolution of calcium oxide (recovery of the catalyst = 64.2%w/w). Lanthanum oxide has a lower catalytic activity in the synthesis of DGDC (yield = 38.4%, selectivity = 54.6%, Entry 2) but the catalyst loss is much less at the end of the reaction (recovery of the catalyst = 98.5%w/w). Magnesium oxide is only partly recovered (yield = 36.4%, selectivity = 52.3%, recovery of the catalyst = 82.3, Entry 3).
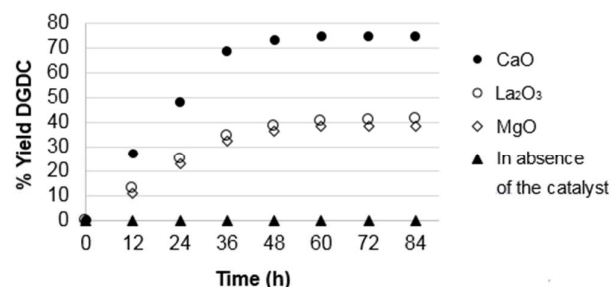

Fig. 3 Kinetic studies of the trans-esterification reaction of diglycerol ether to DGDC using single metal oxides. Reaction conditions: molar ratio DMC:diglycerol ether= 20:1, T=355 K, t=84 h.

Other metal oxides (Entries 4-9, Table 2) are easily and almost quantitatively recoverable, but they show a good activity only in the first of the two steps of the trans-esterification with a 100% selectivity towards the production of 4-[(2,3- di-hydroxy-propoxy)methyl]-1,3-dioxolan-2-one. The analysis of the kinetics shows that an equilibrium position is reached after 60 h, with a yield of 75% using CaO (see Fig. 3). In absence of the catalyst, the reaction does not take place in the same experimental conditions, indicating that is not a thermal reaction. If methanol is eliminated by distillation, the conversion yield can be increased to 85% within 42h, showing that there is an equilibrium shift to right.
Fig. 4 shows that there is a correlation between the acid/basic properties of the metal oxides and their catalytic activity. Increasing the amount of the strong basic sites, an increase of the production of DGDC is observed. These data suggest that this reaction is mainly base-catalyzed. Noteworthy, most of the sites of the catalysts used

(>95%) are strong sites and the catalyst properties practically depend on the strong basic sites.
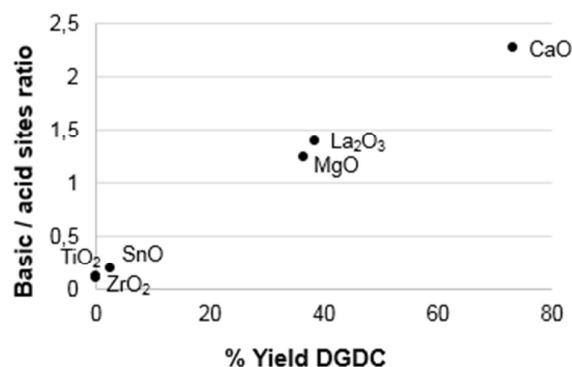

Fig. 4 Correlation between the strong basic/acid sites ratio and the catalytic activity of the metal oxides in the production of DGDC.

3.1.2 Effect of lanthanum in the catalytic activity and the recovery of calcium oxide

Our previous experience with mixed oxides[76-83] has brought us to start a study on the role of such catalysts in the reaction (Table 3). Calcium oxide shows a good activity and selectivity in the production of DGDC (conv. yield= 73.3%, selectivity = 83.8%), but a large part of the catalyst is lost due to the dissolution of the metal oxide in the reaction medium (catalyst recovery = 64.2%w/w). Lanthanum oxide has a lower activity and selectivity in the DGDC synthesis (conv. yield= 38.4%, selectivity = 54.6%), but the catalyst is easily recovered at the end of the reaction cycle (catalyst recovery = 98.5%w/w). To increase the stability of calcium oxide maintaining the same catalytic activity, the effect of lanthanum in the mixed oxide La:Ca was studied in the trans-esterification of diglycerol ether with DMC for DGDC synthesis (Table 3). Entries 2-4 show that increasing the molar ratio La:Ca from 0.1 to 1, a slight decrease of the catalytic activity in the production of DGDC is observed, but the recoverability of the catalyst is noticeably increased. Fig. 5a shows the TPD profiles of CO$_2$ release from mixed oxides La:Ca. It is evident that increasing the molar ratio La:Ca a decrease of strong basic sites (Fig. 5a,b) is observed, that is correlated to the lower production of DGDC (Fig. 5c). The strong basic sites due to Ca present on the surface of mixed oxides La:Ca, play a key role in DGDC production.
However, the presence of the hetero-metal causes an increase of the stability of the calcium oxide. La:Ca = 1 is easily recovered and reused with a good constancy of the catalytic activity, maintaining the same selectivity as CaO (Fig. 6). Interestingly, after 10 cycles the activity of the catalyst is the same as after 5 cycles (Fig. 6) and the elemental analyses of the La:Ca catalyst show that its composition and properties are practically unchanged with respect to the starting material (see the Experimental section). In conclusion, Ca is the most active catalytic site while La acts as a stabilizer of the structure and avoids solubilisation of Ca, preserving, thus, the catalytic activity and assuring a higher surface area (Table 3, Column 3), recoverability and reusability. The catalysts after use do not show any structural change as macroscopically demonstrated by their constant activity in several cycles. (Fig. 6)

Table 3. Effect of the different molar ratio La:Ca in the trans-esterification of diglycerol ether with DMC for the synthesis of DGDC.

	Catalysts		BET Specific Surface Area (m^2/g)	% Conv. diglycerol ether	% DHPMC		% DGDC		%w/w Recovery of the catalysts*
					Yield	Selectivity	Yield	Selectivity	
1	CaO		0.29 ± 0.02	87.5	14.2	16.2	73.3	83.8	64.2
2		0.1	0.35 ± 0.03	85.4	15.0	17.6	70.4	82.4	75.5
3	La:Ca	0.5	0.51 ± 0.02	84.3	16.2	19.2	68.1	80.8	86.3
4		1	0.72 ± 0.04	82.2	15.5	18.8	66.7	81.1	98.1
5	La_2O_3		0.91 ± 0.02	70.4	32.0	45.4	38.4	54.6	98.5

Reaction conditions: molar ratio DMC:diglycerol ether=20:1, weight ratio catalyst:diglycerol ether=20%, T=355 K, t=48 h. *At the end of the reaction, the catalyst was recovered and calcined for 3 h at 773 K.
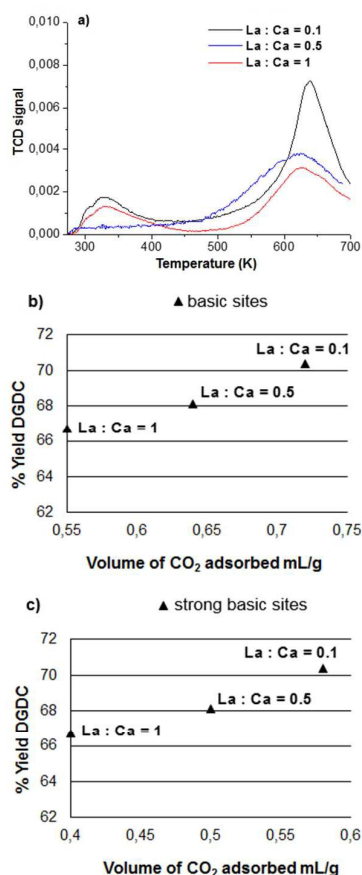

Fig. 5 TPD profiles for CO_2 release from mixed oxides La:Ca and the correlation of the total number of basic sites and strong basic sites to the formation of DGDC.
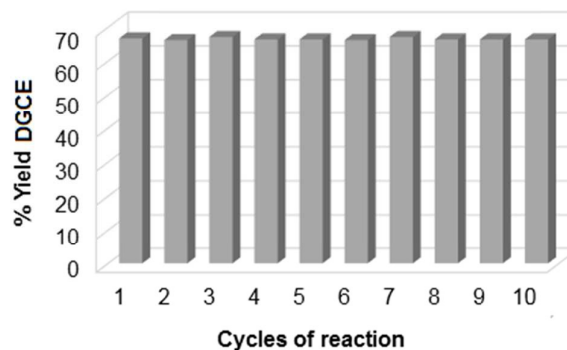

Fig. 6 Recycling tests of the mixed oxide La:Ca=1 in the production of DGDC. Reaction conditions: molar ratio DMC:diglycerol ether=20:1, T=355 K, t=48 h. At the end of the reaction, the catalyst was recovered and calcined for 3 h at 773 K.

3.1.3 Kinetic study using mixed oxide La:Ca = 1 as catalyst in the trans-esterification of diglycerol ether with DMC

In Fig. 7 is reported the kinetic study of the mixed oxide La:Ca = 1 in the trans-esterification reaction of diglycerol ether, compared with the pure oxides. Using lanthanum oxide as catalyst in the trans-esterification reaction a conversion of 40.4% in DGDC is obtained after 60 h of reaction. Increasing the amount of calcium present, an increment of the catalytic activity in the production of the target product is observed with the same catalytic activity revealed for CaO (yield = 75%, Fig. 7). In addition, the catalyst is easily recovered and reused (Fig. 6). For the mixed oxide La:Ca = 1 and CaO, the effect of the different weight ratio (catalyst : diglycerol ether) was also investigated (Fig. 8).
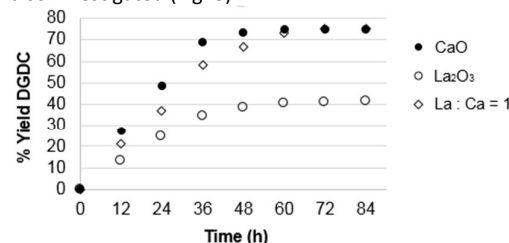
Fig. 7 Kinetic study of the mixed oxide La:Ca=1 in the trans-esterification reaction of diglycerol ether with DMC, compared with pure oxides. Reaction conditions: molar ratio DMC:diglycerol ether=20:1, T=355 K, t=84 h.

Fig. 8 Effect of the different weight ratio (catalyst:diglycerol ether) in the trans-esterification reaction of diglycerol ether with DMC, using CaO and mixed oxide La:Ca=1 as catalysts. Reaction conditions: molar ratio DMC:diglycerol ether = 20:1, T=355 K, t=48 h.

Reducing the amount of the catalyst from 20 to 5%w/w (catalyst : diglycerol ether), a decrease in the production of diglycerol dicarbonate is observed for both catalysts. Conversely, a further increase of the catalyst/substrate ratio does not i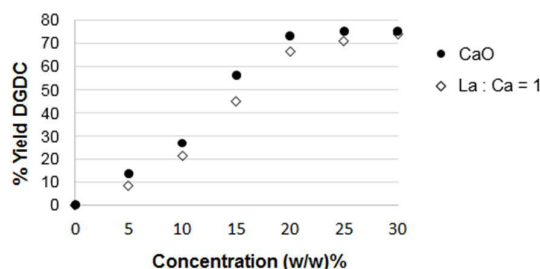mprove too much the conversion yield. At 30%w/w catalyst/substrate ratio the increase is only of 1.5% points from 73.5 to 75%.
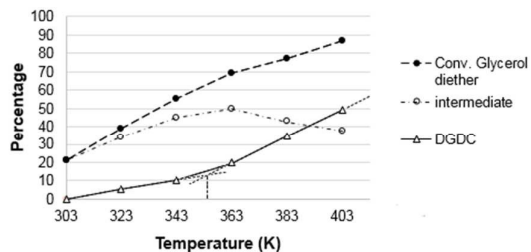

Fig. 9 Effect of the temperature in the trans-esterification of diglycerol ether with DMC using La:Ca=1 as catalyst. Reaction conditions: molar ratio DMC:diglycerol ether=10:1, weight ratio catalyst:diglycerol ether=30%, t=6 h.

3.1.4 Effect of the temperature on the conversion yield and rate

We have investigated the role of the temperature on the reaction and on the conversion rate of the starting glycerol diether into the monocarbonate and the further conversion of the latter into the final DGDC. Fig. 9 shows that around 355 K (the temperature we have used in our tests) the conversion of the intermediate into the final product DGDC undergoes an acceleration with a faster production of DGDC and conversion of the intermediate.A further increase of the temperature may cause the appearance of byproducts, with loss of selectivity. Fig. 9 shows that the conversion of the intermediate into DGDC is the limiting step of the reaction and the temperature strongly influences such reaction. Further studies are in progress in role to gain further knowledge of such two-step reaction.

3.1.5 Comparison of the catalytic activity of the mixed oxide La:Ca = 1 with La_2O_3 and hydrotalcite Mg:Al = 5

Once identified the mixed oxide La:Ca = 1 as the best Ca/La catalyst in the trans-esterification reaction of diglycerol ether with DMC, a comparison was made with La_2O_3 and hydrotalcite Mg:Al (Table 4). These systems are reported in the literature as heterogeneous catalysts for the production of DGDC starting from diglycerol ether and DMC.[72-74]

Mixed oxide La:Ca=1 reveals a higher catalytic activity in the synthesis of DGDC with respect to the other catalysts, in the same experimental conditions. Moreover, the characteristics of the La:Ca heterogeneous catalyst make it possible to set a continuous reactor in which the reagents are flown with the recovery of the product.

3.1.6 Catalytic activity of the mixed oxides La:Zn in the alcoholysis of urea with diglycerol ether

Another approach studied for the production of DGDC was the alcoholysis of urea with diglycerol ether (Eq. 1.2). The alcoholysis of urea offers not only a simple and sustainable route to synthesis of cyclic carbonates, but also a positive economic impact with respect to the use of DMC that is obtained from ethylene carbonate or propylene carbonate, with the production of large amount of glycol as a by-product.[84-87] Zinc oxide is one of the catalysts mostly used

in the synthesis of organic carbonates, however the recovery of the catalyst at the end of the reaction cycle, results very difficult due to the formation of soluble compounds $Zn(NCO)_2(NH_3)_2$.[88-92] To increase the stability of the catalyst maintaining the same catalytic activity, we have studied the effect of lanthanum in the mixed oxides La:Zn. (Table 5).

Zinc oxide shows the best activity in the production of DGDC (yield = 33.1%), but also in this case, the recovery of the catalyst results very difficult due to the dissolution of the metal oxide in the reaction medium (catalyst recovery = 60.2%w/w as $Zn(NH_3)_2(NCO)_2$). Mixed oxide La:Zn=1 shows a good activity in the production of DGDC (yield=20.1%, selectivity=25.7%) and the catalyst is easily recovered and reused. The best catalyst results to be La:Zn=0.1 molar ratio has a conversion yield and selectivity lower than ZnO (yield=29.4%, selectivity=35.8%) with the advantage of a good recoverability (catalyst recovery=83.0%w/w in its original form).

The catalyst La:Zn=0.5 shows the highest recoverability (99%) with a good conversion (80.4%) and a yield of 24.3%.

The presence of the hetero-metal increases the stability of the ZnO catalyst that maintains the same catalytic activity for several cycles of reaction.[75] The reaction is not an equilibrium: in fact, the conversion yield can be improved by prolonging the reaction time (Fig. 10).

Table 4. Comparison of the catalytic activity of the mixed oxide La:Ca = 1 with La_2O_3 and hydrotalcite Mg:Al = 5 in the same reaction conditions.

	Catalysts	% Conv. diglycerol ether	%DHPMC		% DGDC	
			Yield	Selectivity	Yield	Selectivity
1	La:Ca = 1	86.9	37.5	43.1	49.4	56.9
2	Hydrotalcite Mg:Al = 5	80.5	48.1	59.8	32.4	40.2
3	La_2O_3	77.4	44.8	57.9	32.6	42.1
	No catalyst	12.4	12.4	100	0	0

Reaction conditions: molar ratio DMC:diglycerol ether=10:1, weight ratio catalyst:diglycerol ether=30%, temperature=403 K, time=6 h

Table 5. Effect of the different molar ratio La:Zn in the alcoholysis of urea with diglycerol ether for the synthesis of DGDC.

	Catalysts		% Conv. diglycerol ether	% DHPMC		% DGDC		%w/w Recovery of the catalysts*
				Yield	Selectivity	Yield	Selectivity	
1	ZnO		84.6	51.5	60.9	33.1	39.1	60.2
2		0.1	82.1	52.7	64.2	29.4	35.8	83.0
3	La:Zn	0.5	80.4	56.1	69.8	24.3	30.2	99.0
4		1	78.2	58.1	74.3	20.1	25.7	95.4
5	La_2O_3		77.4	59.0	76.2	18.4	23.8	96.6
	No catalyst		53.4	53.4	100	0	0	-

Reaction conditions: molar ratio urea:diglycerol ether=2:1, weight ratio catalyst:diglycerol ether=20%, T=423 K, t=15 h, under vacuum 20 Pa. *At the end of the reaction, the catalyst was recovered and calcined for 3 h at 773 K.
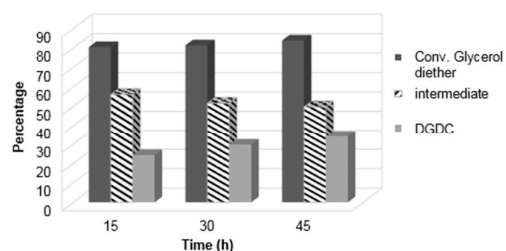
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Fig. 10 Effect of the reaction time in the alcoholysis of urea with diglycerol ether using La:Zn = 0.5 as catalyst. Reaction conditions: molar ratio urea:diglycerol ether=2:1, weight ratio catalyst:diglycerol ether =20%, T=423 K, under vacuum 20 Pa.

Fig. 10 shows that increasing the reaction time, the conversion of glycerol diether increases together with the formation of DGDC, while the intermediate decreases. The reaction goes to completion within 72 h, clearly showing that it is not an equilibrium reaction.
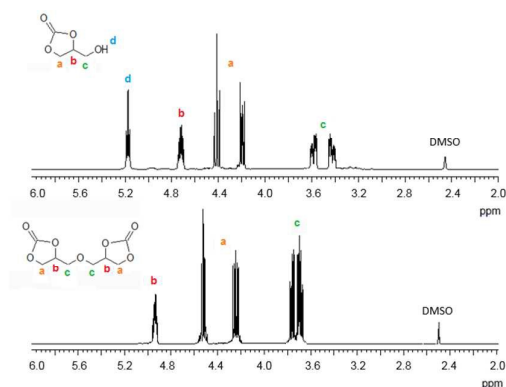

Fig. 11 Comparison of the ^{1}H NMR spectrum of glycerol carbonate with that of DGDC.

3.1.7 Isolation and characterization of diglycerol dicarbonate

As reported in 2.3.3, the isolation of DGDC from the reaction mixture was made by crystallization. In Figs. 11-12 are shown, respectively, the ^{1}H and ^{13}C NMR spectra of DGDC isolated from the trans-esterification process, compared with glycerol carbonate.

From the analysis of NMR spectra, it is possible to observe the absence of the hydroxylic group of glycerol carbonate. The bidimensional NMR spectrum definitively confirms the structure of the DGDC (Fig. 13), as clearly shown by the H-C correlation.

This represents the first full characterization of such compound as the literature gives only a partial information about its characterization in solution.[72-74]

3.2 Diglycerol tricarbonate

3.2.1 Catalytic activity of single metal oxides in the trans-esterification reaction of glycerol carbonate to afford DGTC

Table 6 shows the catalytic activity of single metal oxides in the trans-esterification of glycerol carbonate with DMC for the synthesis of DGTC (Eqs. 1.3-1.4).

Calcium oxide shows the best catalytic activity with a yield of 15.4%. However, also in this case, the recovery of the catalyst was very difficult due to the leaching of the catalyst in solution (catalyst recovery = 67.2%w/w). The study of the basic/acid properties of the metal oxides has highlighted a correlation between the basicity and

the catalytic activity of the catalysts (Fig. 14). Similarly, to the case of DGDC (Fig. 4), the data suggest that this process also is mainly base-catalyzed.
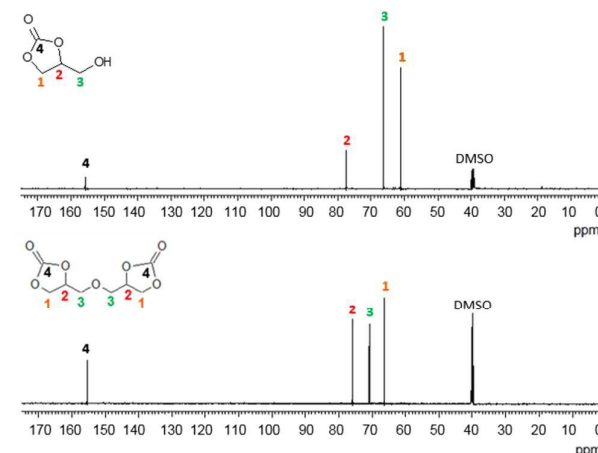

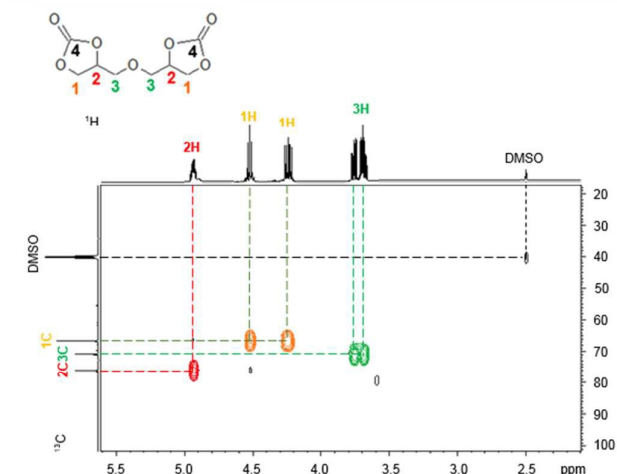Fig. 12 Comparison of ^{13}C NMR spectra of glycerol carbonate and DGDC

Fig. 13 Bidimensional NMR spectrum of DGDC

In an attempt to increase the reaction yield, the trans-esterification reaction of MGC with glycerol carbonate was also investigated (Eq. 1.5, Table 7). The reaction proceeds to a conversion of MGC to 73.5%, but the yield of DGTC is only 16.9% with a selectivity of 23%. Moreover, the GC-MS analysis reveals the production of DMC during the reaction. The presence of DMC indicates that the synthesis of DGTC occurs with a different mechanism of reaction that may not imply the reaction of glycerol with MGC. In order to explain what happens in such reaction, a study of the activity of the metal oxides was carried out in presence of only MGC as reagent.

3.2.2 Disproportionation reaction of MGC

In Table 8 is reported the catalytic activity of single metal oxides in the disproportionation reaction of MGC (Eq. 1.6).
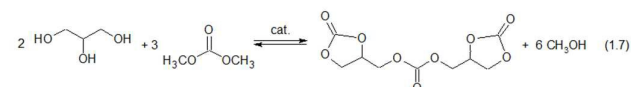
Table 6. Comparison of the catalytic activity of single metal oxides in the reaction of trans-esterification of glycerol carbonate with DMC.

	Catalysts	% Conv DMC	% MGC		% DGTC		%w/w recovery of the catalysts
			yield	selectivity	yield	selectivity	
1	CaO	58.1	42.7	73.5	15.4	26.5	67.2
2	La$_2$O$_3$	50.5	40.7	80.6	9.8	19.4	97.3
3	MgO	45.3	37.9	83.7	7.4	16.3	85.4
4	SnO	30.2	28.9	95.7	1.3	4.3	96.2
5	TiO$_2$	20.4	20.4	100	0	0	97.1
6	ZrO$_2$	18.4	18.4	100	0	0	97.4
7	Nb$_2$O$_5$	16.8	16.8	100	0	0	96.9
8	No catalyst	14.2	14.2	100	0	0	-

Reaction conditions: molar ratio glycerol carbonate:DMC=5:1, weight ratio catalyst:DMC=20%, T=413 K, time=24 h. *At the end of the reaction the catalyst, was recovered and calcined for 3 h at 773 K.
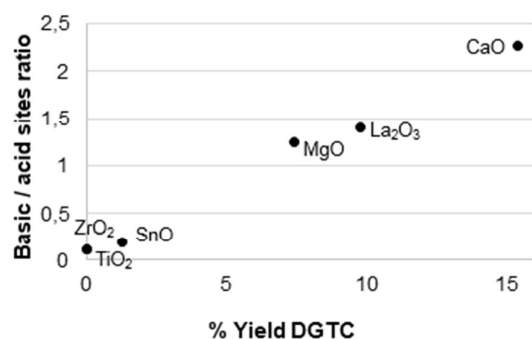

Fig. 14 Correlation between the basic/acid sites ratio and the catalytic activity of single metal oxides in the production of DGTC.

Table 7. Catalytic activity of single metal oxides in the trans-esterification of glycerol carbonate with MGC.

	Catalysts	% Conv. glycerol carbonate	% DGTC		%w/w Recovery of the catalysts*
			Yield	Selectivity	
1	CaO	73.5	16.9	23.0	64.3
2	La$_2$O$_3$	68.1	11.7	17.2	97.1
3	MgO	60.4	10.1	16.7	82.3
	No catalyst	34.1	1.3	3.8	-

Reaction conditions: molar ratio MGC:glycerol carbonate=2:1, weight ratio catalyst: MGC=20%, T=413 K, t=24 h. *At the end of the reaction, the catalyst was recovered and calcined for 3 h at 773 K.

**Table 8.** Catalytic activity of single metal oxides in the disproportion reaction of MGC.

	Catalysts	% Conv. MGC	% Yield DMC	% Yield DGTC	%w/w Recovery of the catalysts*
1	CaO	42.5	21.3	21.2	67.3
2	La$_2$O$_3$	33.2	16.6	16.6	97.4
3	MgO	25.4	12.6	12.8	83.2
	No catalyst	5.6	2.8	2.8	-

Reaction conditions: weight ratio catalyst:MGC=20%, T=413 K, t=24 h. *At the end of the reaction, the catalyst was recovered and calcined for 3 h at 773 K.

From the data analysis, it is possible to observe how the key step for the synthesis of DGTC is represent by the disproportionation of MGC. In fact, MGC alone reacts using CaO as catalyst with a yield of 21.2% in DGDC. DGTC and DMC are formed in equimolar amounts, as revealed by GC-MS. The conversion yield is not very high but the selectivity is 100% towards DGTC (Eq. 1.8).

3.2.3 Comparison of the catalytic activity of the mixed oxide La:Ca = 1 with K$_2$CO$_3$

To increase the stability of calcium oxide, the mixed oxide La:Ca = 1 was tested in the disproportionation of MGC and compared with K$_2$CO$_3$ (Table 9) reported in literature to act as catalyst for the synthesis of DGTC starting from glycerol and DMC.[71] Mixed oxide La:Ca = 1 shows a catalytic activity better than K$_2$CO$_3$ in the same experimental conditions.
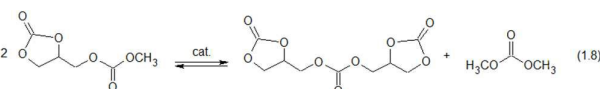
Table 9. Comparison of the catalytic activity of the mixed oxide La:Ca = 1 with K$_2$CO$_3$.

	Catalysts	% Conv. MGC	% Yield DGTC	%w/w Recovery of the catalysts*
1	La:Ca = 1	37.4	18.7	96.9
2	K$_2$CO$_3$	13.4	6.7	-

Reaction conditions: weight ratio catalyst:MGC=20%, T=413 K, t=24 h. *At the end of the reaction, the catalyst was recovered and calcined for 3 h at 773 K.
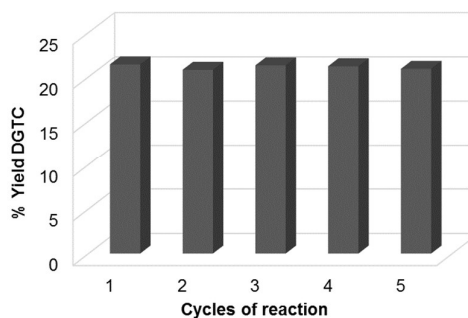

Fig. 15 Recycling tests of the mixed oxide La:Ca=1 in the production of DGTC. Reaction conditions: weight ratio catalyst:MGC=20%, T=413 K, t=24 h. *At the end of the reaction, the catalyst was recovered and calcined for 3 h at 773 K.

An aspect to consider is that our heterogeneous catalyst is easily recovered at the end of the reaction cycle and reused without loss of the catalytic acitivity (Fig. 15).

Conclusions

In this work, bi-metallic oxides based on La, Ca, Zn were synthesized and used as catalysts, in eco-friendly routes for the synthesis of DGDC and DGTC. The trans-esterification reaction of diglycerol ether with DMC, resulted to be the best method for the synthesis of DGDC.

Different catalysts were tested, characterized by different acid/basic sites ratio. Mixed oxide La:Ca molar ratio 1 shows a good catalytic activity in the production of DGDC (yield = 66.7%) with a high selectivity (81.1%).

Respect to calcium oxide alone, or lanthanum oxide or else hydrotalcite Mg:Al = 5, the La:Ca catalyst shows the highest yield, is more easily recoverable and reusable, with a very moderate loss of the catalytic activity. For the DGTC synthesis, we have shown that the disproportionation of MGC is the key step (CaO as catalyst, yield 21.1% and selectivity of 100%), more than the reaction of DMC with two molecules of glycerol carbonate. The mixed oxide La:Ca = 1 afforded much better yield (19.9) and selectivity (100%) than K_2CO_3 (6.7%) described in the literature. Mixed oxides were also easily recovered and reused.

Acknowledgements

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