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Enhanced use of renewable resources: Transesterification of glycerol catalyzed by hydrotalcite-like compounds

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ABSTRACT

The increase in bio-diesel production is generating high quantities of glycerol as by-product. Glycerol carbonate and its esters are key multifunctional compounds employed as chemical intermediates, monomers, solvents, additives and fuel contents. In this study, glycerol carbonate and glycerol dicarbonate were synthesized as glycerol value-added products *via* a transesterification reaction using diethyl carbonate as co-substrate. This green, efficient and selective process involved catalysis with different hydrotalcite-like compounds containing a Mg/Al molar ratio of 4 that were activated by calcination and by calcination followed by rehydratation under ultrasound. The correlation between the basic properties of the solid catalysts and the activity in the glycolysis reaction was investigated. The catalytic activity shown by the different activated Mg/Al solids was not proportional to the number of basic sites present in the catalyst. The highest activity was found for the rehydrated hydrotalcite catalyst, which showed basic Brønsted sites and which can be reused several times without significant loss of activity.

1. Introduction

Environmental and political concerns are generating growing interest in renewable alternative fuels such as bio-diesel produced from vegetable oils by transesterification. The high co-production of glycerol, however, linked to this production (over 100 g/kg of bio-diesel) represents a considerable technical and economic burden. On the one hand, glycerol is not fully exploited on the market, which is even more so with the increase in the production and use of bio-diesel; on the other hand, the presence of residual glycerol, as such and as mono-, di- and triglycerides, in bio-diesel is not tolerated, due to problems of de-mixing and fouling. Narrow specification ranges have been then established fixing the free glycerol content in bio-diesel lower than 0.02% by weight, and the total glycerol, i.e. both in free form and partially or totally esterified, lower than 0.25% by weight. Complex separation and purification operations are therefore required to meet these specifications. After refining, it can reach high-purity grade for pharmaceutical and industrial uses. However, the price of glycerol is being pushed down as supplies increase as a result of increased bio-diesel production [1]. Therefore, it is especially important to explore new applications for this product as well as alternative strategies for transforming it into new suitable products. Glycerol carbonate (4-hydroxymethyl-1,3-dioxalan-2-one) and its esters are very interesting derivates of glycerol. They are relatively new materials in the chemical industry and have great potential as a new component in gas-separation membranes, in non-volatile solvents for dyes, lacquers, pharmaceuticals, detergents, adhesives, cosmetics, and biolubricants [2], and for the synthesis of new functionalized polymers such as polyglycerol [3]. Fuels represent large scale applications, and Notari and Rivetti et al. [4] recently reported that a mixture containing alkyl esters or fatty acids (bio-diesel) and one or more esters of fatty acids of glycerol carbonate (constituting between 10 and 40% of the weight) can be used as fuel.

The present industrial synthesis of glycerol carbonate involves two steps [5], as illustrated in Scheme 1: first ethylene oxide reacts with carbon dioxide to yield the cyclic ethylene carbonate which then reacts further with glycerol to yield glycerol carbonate and ethylene glycol.

The improvement of the economic and environmental feasibility of the industrial synthesis of glycerol carbonate (i.e. reducing the number of steps and waste) entails the obtaintion of an optimized direct method for its production. Few references have been found in the literature concerning the production of glycerol carbonate using simplified methodologies. Vieville et al. [6] obtained glycerol carbonate (up to 32% after 1 h) by direct carbonation of glycerol

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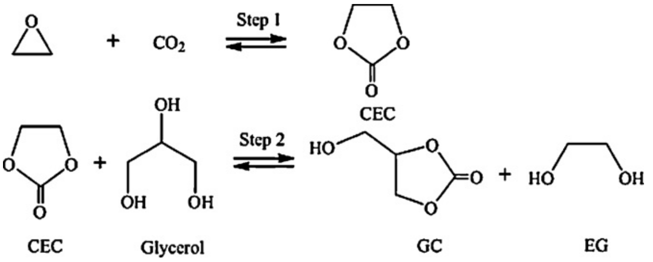


Scheme 1. Industrial synthesis of glycerol carbonate.

in supercritical carbon dioxide in the presence of zeolites and ion exchange resins, using ethylene carbonate as co-reactant. Aresta et al. have recently reported the direct carboxylation of glycerol with carbon dioxide using tin complexes (n-$Bu_2Sn(OCH_3)_2$, n-Bu_2SnO and $Sn(OMe)_2$) as catalysts [7]. However, the best glycerol conversion achieved after 15 h of reaction was below 7%. Catalysts based on zinc, $Zn(CH_3C_6H_4\text{-}SO_3)_2$, were used by Yoo et al. [8] to synthesize glycerol carbonate from glycerol and urea. In this case, the conversion achieved was 85% after 1 h of reaction.

The non-toxicity, biodegradability and cleaner production process of alkyl carbonates such as dimethyl or diethyl carbonate (DMC or DEC, respectively) make them green reagents that prevent pollution at the source during synthesis [9]. Moreover, since DEC includes ethoxy and carbonyl groups, it can be used as an effective carbonylating and ethylating agent as well as a raw material for manufacturing polycarbonates [10]. Glycerol carbonate can be obtained via a transesterification reaction of DMC with glycerol using homogeneous catalysts such as n-$Bu_2Sn(OCH_3)_2$, resulting in a 65% conversion after 15 h [7]. The usual synthesis uses as a catalyst large quantities of a Brønsted base, K_2CO_3; to produce either glycerol carbonate, glycerol dicarbonate or diglycerol tricarbonate depending on the reaction temperature and/or the amount of DMC added [3]. Mouloungui et al. [11] reported the synthesis of glycerol carbonate by reaction of glycerol on a cyclic organic carbonate in the presence of a solid catalyst consisting of an anionic, bi-carbonated or hydroxylated, macroporous resin, or alkaline X- or Y-type zeolite. This reaction produces glycol as by-product with a selectivity of about 15–30%. To the best of our knowledge, only one patent has been published regarding the use of basic solids (commercial Mg/Al-hydrotalcite Macrosorb CT 100) as heterogeneous catalysts for the conversion of glycerol. This produced a mixture of oligomers containing only 23% glycerol carbonate [12].

Hydrotalcite-like compounds have the general formula $[M^{II}{}_{1-x}M^{III}{}_{x}(OH)_2]^{x+}A^{n-}{}_{x/n}\cdot nH_2O$, where M^{II} and M^{III} stand for a divalent and a trivalent cation, respectively, and A is a charge-balancing anion. The structure consists of brucite-like layers $[Mg(OH)_2]$ with edge-sharing hydroxyl octahedra occupied by Mg^{II} cations. In hydrotalcites, some divalent cations are isomorphically substituted by trivalent ones which introduce a positive charge that is balanced by anions located in the interlayer. Additionally, crystallization water molecules are also found in the interlayer [13]. They are usually prepared by co-precipitation from metal salts in alkaline media at constant pH followed by a hydrothermal treatment of the precipitate. The usual protocol of activation for these materials is controlled thermal decomposition which leads to the formation of mixed oxides showing a good dispersion of metals, a large specific surface area and Lewis basic properties. The rehydration of calcined hydrotalcites under a CO_2 free atmosphere allows the layered structure to be recovered containing interlayer OH^- anions, which provides significant Brønsted basic properties [14,15]. The basic properties of the solid can be tuned by the procedure of rehydration: Roelofs et al. [16] reported a higher activity after hydration, followed by washing with ethanol. The higher activity in base catalyzed reactions has been reported when they are activated by thermal decomposition followed by rehydration processes using ultrasounds [17,18]. Cantrell et al. showed that the Brønsted basic sites of rehydrated Mg–Al hydrotalcites are effective catalysts for the transesterification of tributyrin with methanol, with an increase of the rate with the Mg content in the Mg–Al hydrotalcites [19].

We report here the results of an exploratory study focussed on the synthesis of glycerol carbonate by the transesterification reaction of glycerol with DEC. Due to the report of Cantrell [17], a Mg–Al hydrotalcites with Mg/Al molar ratio of 4 was selected as catalyst, since it is known that phase separation occurs above this ratio.

2. Experimental

2.1. Catalyst preparation

Parent Mg/Al-hydrotalcite-like precursor with a molar ratio of 4 was obtained according to the standard co-precipitation method as follows. The appropriate amounts of $Mg(NO_3)_2\cdot 6H_2O$ and $Al(NO_3)_3\cdot 9H_2O$ were dissolved in 150 cm^{-3} of distilled water and added dropwise into a glass vessel which initially contained 200 cm^{-3} of deionized water. The pH was controlled by adding a 2 M NaOH solution and was kept at 10. Both solutions were mixed under vigorous stirring. The suspension was stirred overnight at room temperature. The precipitated solid was filtered and washed several times with water and dried at 110 °C to yield the as-synthesized hydrotalcite (HT-as). The solid was calcined in air by heating at 10 °C/min up to 450 °C over 3 h to obtain the corresponding mixed oxides. This solid was named HTO4, where 4 refers to Mg/Al molar ratio). A part of the mixed oxide was reconstructed back in decarbonated water by sonication for 1 h under an inert atmosphere to maximize the accessibility of the OH^- groups [17,18]. This sample was called HTr4.

2.2. Catalysts characterization

Mg and Al elemental chemical analyses were obtained by atomic absorption spectroscopy (AAS) using a PerkinElmer 703 instrument, before the samples were dissolved in HNO_3. Specific surface areas were determined by nitrogen adsorption at −196 °C using a Micromeritics ASAP 2000 equipment. Samples were previously degassed in situ at 120 °C under vacuum. Surface areas were calculated using the Brunauer–Emmet–Teller (BET) methods over a P/P_0 range where a linear relationship was maintained. X-ray diffraction (XRD) powder patterns were collected on a Siemens EM-10110BU diffractometer model D5000 fitted with a Cu Kα (1.541 Å) radiation source. Data were recorded over a 2θ range of 5–70° with an angular step of 0.05° at 3 s/ step which resulted in a scan rate of 1°/min. Patterns were identified using files from the Joint Committee on Powder Diffraction Standards (JCPDS).

The basicity measurements were obtained by temperature-programmed desorption (TPD) of CO_2 on a Thermo Finnigan TPDRO 1100 equipped with a TCD detector. Typically, ca. 0.150 g of sample were placed in a tubular quartz reactor. The sample was pretreated with Ar at 80 °C during 1 h and then cooled to room temperature and treated with a CO_2 flow (3% CO_2 in He). The desorption of CO_2 was measured by heating the sample from room temperature to 800 °C at a heating rate of 10 °C/min in He flow. Water was trapped on magnesium perchlorate. The number of basic sites was calculated from the CO_2 peaks by deconvolution using the software of the equipment, and a calibration of the instrument using a known amount of $CaCO_3$. Thermogravimetric analysis (TGA) curves were recorded in a Labsys/Setaran TG thermo balance apparatus from room temperature to 900 °C, at a heating rate of 10 °C/min.

Table 1
Characterization of catalysts. Chemical composition, PXRD analysis and BET surface areas.

Catalyst	Elemental analysis[a]		PXRD analysis			Surface area[c] ($m^2 g^{-1}$)
	M(II)/M(III)	x	$d_{(003)}$ (Å)	$d_{(110)}$ (Å)	a (Å)	
HT-as	4.29 (4)[b]	0.19	8.01	1.53	3.07	17
HTO4	4.29		–	–	4.19	199
HTr4	4.08	0.19	7.67	1.53	3.06	57

[a] Atomic absorption spectroscopy.
[b] Nominal value.
[c] Using BET method.

2.3. Standard batch catalytic transesterification reaction

Glycerol (99%) and DEC (99.5%, GC grade) were purchased from Aldrich and used without any further purification. Ethanol HPLC grade from Aldrich was used as a solvent to characterize the products obtained. Transesterification reactions were performed in a three-neck round bottomed flask equipped with a condenser. Typically, the flasks were charged with an excess of DEC (38.95 g) and glycerol (1.85 g). Freshly activated catalyst (0.3 g) was added and the experiment started with mechanical stirring under argon at 130 °C. Stirring was continued until the completion of the reaction. Aliquots were periodically withdrawn, filtered and quantified by GC–MS analysis. This was performed on a Shimadzu GC–MS (QP 2010) with a Zebron ZW-WAX capillary column.

2.4. Recycling experiments

We investigated the reuse of the catalyst HTr4 in the transesterification reaction of glycerol with DEC under the same reaction conditions that were used for the standard transesterification reaction. The reaction mixture was removed with a syringe equipped with a microfilter when the reaction had finished, leaving the catalyst in the smallest possible amount of liquid. The reaction mixture was then washed twice with DEC. After that, a new charge of reactants was added to the used catalyst and the next run was performed.

3. Results and discussion

3.1. Characterization and basic properties of the solids

Table 1 gives the results of the chemical analysis of the metals in the samples. The Mg/Al atomic ratio for the as-synthesized hydrotalcite was slightly higher than the atomic ratio fixed in the solution. Generally, the optimal value of x for a pure LDH phase ranges from 0.2 to 0.33 [20]. However, pure lamellar phases are reported for values of $x = 0.15–0.34$ in MgAl-LDHs [19,21]. X-ray diffraction patterns (not shown) exhibited single phases consistent with a hydrotalcite structure.

The XRD pattern of the HT-as sample exhibited symmetric reflections corresponding to the (0 0 3), (0 0 6) and (0 0 9) planes and recorded at 8.01, 4.03 and 2.63 Å, respectively. The indexing was based on rhombohedral symmetry (polytype 3R) [21]. The value of the lattice parameter a, 3.07 Å, was calculated as twice the spacing of plane (1 1 0) whose maximum was recorded close to $2\theta = 60^\circ$ and is characteristic of hydrotalcite-like compounds, (JCPDS 22-700). The value of parameter a is in the range of that observed for pure hydrotalcite phases with low Al content [18,22]. After calcination at 450 °C, the layered structure was destroyed and the calcined sample presented the typical features of Mg(Al)Ox mixed oxide (HTO), whose reflections appeared at $2\theta = 43^\circ$ and 63°, thus corresponding to a periclase-like structure (JCPDS 87-0653). Its structural parameters are lower than those in the pure MgO rock salt-type structure, showing that Al^{3+} cations are inserted into the structure [23,24]. The original layered structure was recovered from the calcined material after rehydration in the absence of CO_2. The sample presented a meixnerite structure (JCPDS 35-0965) because of the well-known “memory effect” [25] where the original nitrate anions have been replaced by Brønsted OH sites. The most striking feature of the rehydrated sample was the increased intensity of the basal peaks in the rehydrated samples compared with the original hydrotalcite. This indicates an increase in crystallinity, despite the ultrasound treatment for rehydration, which agrees with data obtained from N_2 adsorption. Rehydration in water could provoke a dissolution of the smaller particles and increase of the larger ones (Ostwald ripening) which could account for this increase of crystallinity. The BET specific surface area for the as-synthesized hydrotalcite was in accordance with those reported in the literature [15]. It can be noticed that the surface area increased from about 17 $m^2 g^{-1}$ for the as-synthesized sample to 200 $m^2 g^{-1}$ for the calcined sample, and decreased to 57 $m^2 g^{-1}$ after rehydration, in spite of the use of ultrasounds.

TGA of as-synthesized and rehydrated samples is displayed in Fig. 1. Both samples exhibited the two characteristic steps of weight loss for hydrotalcite-like compounds [26]. A first weight loss of 11.2% in the HT-as sample was observed from about 120 to 250 °C and is caused by the elimination of adsorbed and interlayer water. A second weight loss of approximately 25.8% in the temperature range of 380–700 °C was caused by the loss of hydroxyl groups in the brucite layers and interlayer anions. The first weight loss was greater in the meixnerite-like compound than in the as-synthesized sample, which suggests that the former has more adsorbed water molecules. From the second weight loss, the rehydration degree could be estimated by comparing it with the theoretical weight loss in meixnerite-type materials. The rehydrated sample exhibited a second weight loss of 20.4% (6% lower than the as-synthesized sample), which indicates an incomplete rehydration of the mixed oxide, with a degree of reconstruction of 84.4%.

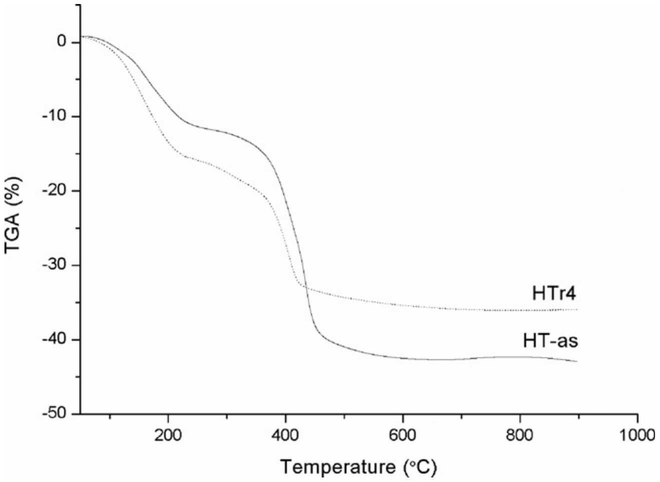


Fig. 1. Thermogravimetric analysis of the hydrotalcite samples.

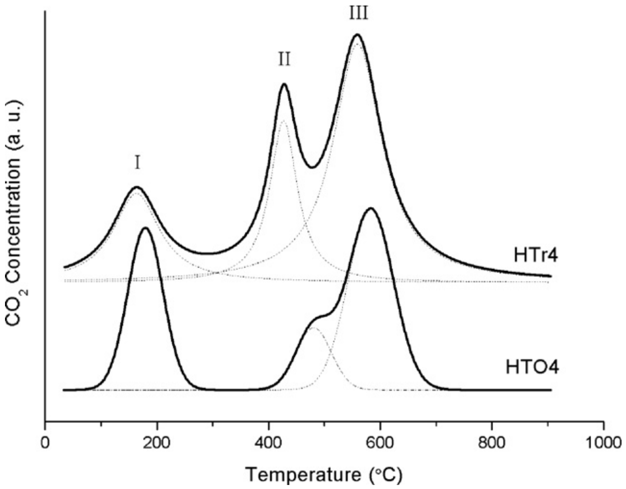


Fig. 2. CO_2 losses during temperature-programmed desorption experiments.

The basicity of the mixed oxide and rehydrated catalysts was measured by TPD-CO_2 and the basic strength could be assigned according to the temperature at which peaks appeared (Fig. 2). The number of basic sites was estimated by integration of these peaks. A recent calorimetric investigation of CO_2 adsorption, showed a non-uniform surface for the mixed oxide, and very close values for the differential heats of adsorption on MgO and hydrotalcites activated at 400 °C [27].

Hydrotalcite looses both water and CO_2 at about 400 °C [25], and since the second peak around 440 °C is more intense on the rehydrated catalyst, it can be assigned to the decomposition of bicarbonate species, formed by adsorption of CO_2 on the Brønsted basic sites. The third broad peak between 480 and 650 °C is observed at the same position on the both calcined and rehydrated samples. This peak could be ascribed to the strong Lewis sites identified to O^{2-} linked to Al or to low coordinatively unsaturated Mg species (corners or edges). The low temperature peak at 150 °C, is more intense on the calcined sample; it can be assigned to an adsorption on Lewis sites identified to oxygens linked to Mg cations localised on basal planes.

Table 2 shows the similarity in the number of basic sites measured by the adsorption of CO_2 for both HTr4 and HTO4. The main difference is a higher number of Brønsted basic sites on the rehydrated sample HTr4. The investigation of CO_2 adsorption by calorimetry [28] indeed showed that rehydration did not affect the total number of sites, but decreased the strength, which agrees with the present results.

3.2. *Study of the transesterification reaction of glycerol in batch*

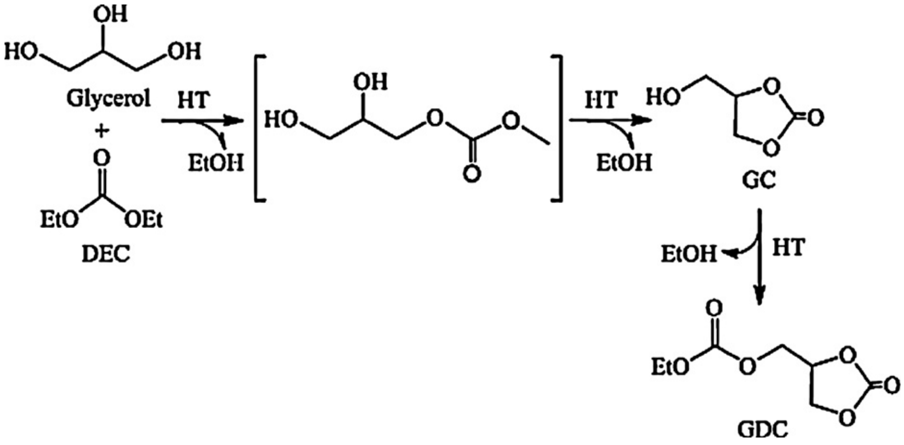
The transesterification reaction of glycerol with DEC was investigated using the mixed oxide and rehydrated sample from different hydrotalcite-like materials as catalysts (Scheme 2).

The transesterification was performed at 403 K under a small flow of Ar with a molar excess of DEC (17:1) to shift the reaction equilibrium towards the products. The catalytic properties were determined by measuring the glycerol conversion *versus* time (Fig. 3). The rehydrated catalyst HTr4 presented a 99% glycerol conversion after 10 h of reaction, whereas the mixed oxide catalyst HTO4 achieved only a 76% glycerol conversion after 50 h of reaction. If we take into account the similar total number of basic sites of these solids and the significantly lower surface area of the rehydrated sample compared to the mixed oxide (57 and 199 m^2/g, respectively), HTO4 (with Lewis basic sites) shows definitively poorer catalytic properties than HTr4 (with Brønsted basic sites) (Table 2). This behaviour suggests that, in terms of activity, the accessibility and the number of base sites is not as important as the type of basicity of the solid, as has been observed in the literature [29]. The presence of Brønsted basic sites in the HTr4 catalyst induces a better catalytic activity in the transesterification reaction of glycerol than the HTO4 catalyst, which has a similar quantity

Table 2
Results of basic properties for the catalysts.

Sample	TPD analysis of adsorbed CO_2			Total evolved CO_2 (μmol g^{-1})
	Desorption peaks			
	I (150–160 °C)	II (400–500 °C)	III (550–600 °C)	
HTO4[a]	94	19	61	174
HTr4[a]	29	64	146	189

[a] Fresh catalyst.



Scheme 2. Consecutive hydrotalcite-catalyzed transesterification reaction of glycerol with DEC.

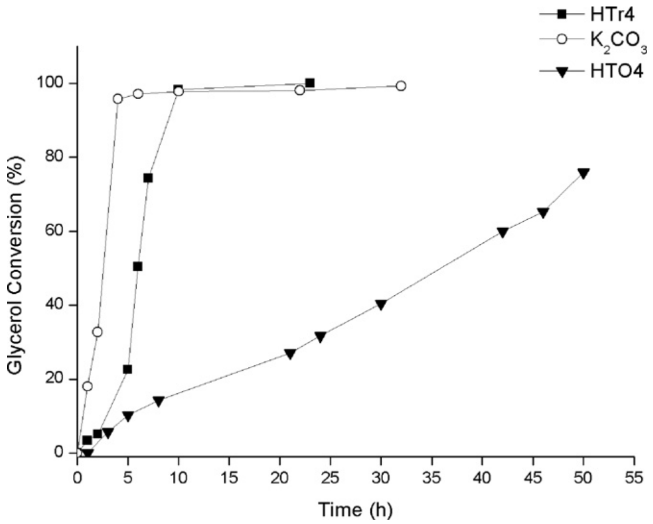


Fig. 3. Conversion of glycerol *vs.* reaction time.

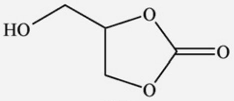
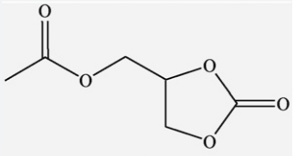
of Lewis basic sites. This is probably because the Brønsted basic sites are better at extracting the proton from the alcohol (which presents higher acidity compared with DEC) thus providing the alkoxide anion stabilized at the surface of the solid.

On the other hand, it should be remembered that the three hydroxyl groups of glycerol can be used for the transesterification reaction. Under the reaction conditions, the primary alcohols are presumably more reactive than the secondary alcohol. However, once the transesterification of the primary alcohol occurs, the intramolecular reaction between the secondary alcohol and the nearby carbonate group is favoured, thus producing glycerol carbonate. Finally, the transesterification reaction between the glycerol carbonate and the DEC leads to the formation of glycerol dicarbonate, or GDC (Scheme 2).

The different catalysts used in the transesterification reaction of glycerol led to different products (see Table 3). The mixed oxide catalyst HTO4 did not lead to any reaction between the diethyl carbonate with the third OH group of glycerol. The only product obtained was glycerol carbonate after 54 h of reaction (Entry 1, Table 3). By contrast, the HTr4 sample catalyzed the reaction and, after 10 h, converted almost all the glycerol to carbonate with a selectivity of 33% to glycerol dicarbonate. After 54 h of reaction, 83% of the glycerol carbonate was transformed into glycerol dicarbonate (Entry 2, Table 3).

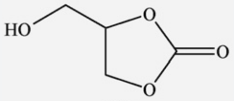
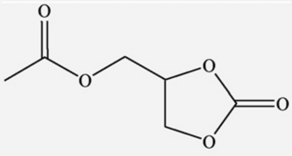
The homogeneous catalyst K_2CO_3 was also tested under the same reaction conditions when reacting glycerol with DEC. The number of Brønsted basic sites introduced into the homogenous reaction was comparable to the number of Brønsted basic sites found on the HTr4 sample. This catalyst presented a slightly higher activity than the rehydrated catalyst HTr4, giving a conversion of

Table 3
Synthesis of glycerol carbonate or dicarbonate from glycerol under standard conditions with different catalysts.

Entry	Catalyst[a]	Reaction time (h)	Glycerol converted (%)[b]	Yield (%) [b]  GC	Yield (%)[b]  GDC
1[c]	HTO4	50	76	76	–
2[c]	HTr4	10	98	65	33
		29	99	23	76
		54	99	17	82
3	K_2CO_3	10	98	44	54
		32	99	53	46

[a] All the reactions were performed under standard conditions.
[b] Conversions were determined by GC/MS.
[c] 0.3 g of solid catalyst that corresponds to 20 μmol of Brønsted sites.

Table 4
Recycling of HTr4.

Run[a]	Reaction time (h)	Glycerol converted (%)	Yield (%)[b]  GC	Yield (%)[b]  GDC
1	10	98	65	33
	54	99	17	82
2	54	99	34	65
	60	99	31	68
3	60	97	93	4

[a] All the reactions were performed under standard conditions using HTr4 as catalyst.
[b] Conversions were determined by GC/MS.

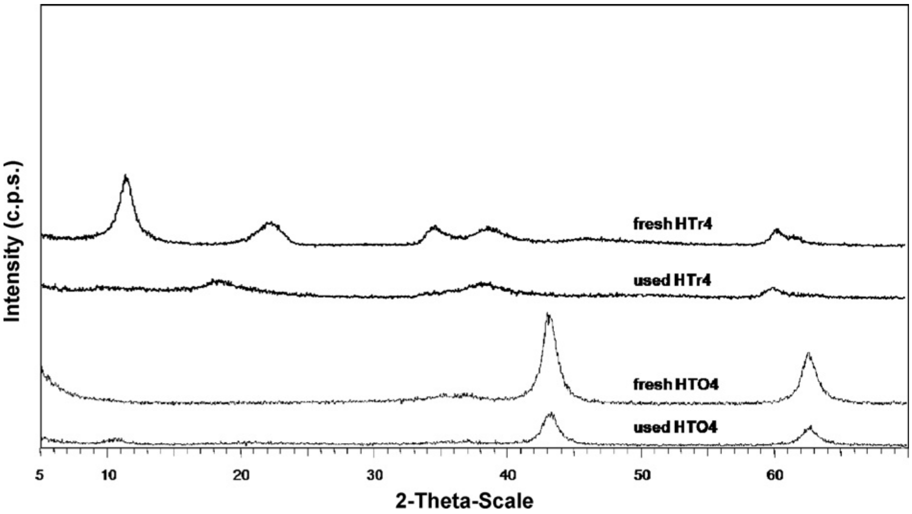


Fig. 4. PXRD patterns for fresh and used catalysts.

97% after 6 h of reaction. However, the maximum GDC achieved was only 53% (Entry 3, Table 3).

3.3. Recycling experiments

The reuse of the catalyst was investigated in the transesterification reaction of glycerol with DEC with the most active catalyst, HTr4 (Table 4). During the experiment, the activity in the consecutive cycles decreased: the time required to reach full conversion 99% of glycerol was 10 h in the first run, and 24 h in the second consecutive run. The third consecutive run reached 97% conversion after 60 h. The same trend was observed for the transesterification of glycerol carbonate with DEC to obtain glycerol dicarbonate. In this case, after 54 h of reaction, the first run gave an 82% GDC conversion which decreased dramatically in the following runs, yielding only a 4% after 60 h of reaction in the third consecutive run.

An attempt was done to investigate the structure of the catalyst after reaction, determining the XRD pattern of the catalyst (Fig. 4). The analysis revealed a loss of the crystalline structure of the original meixnerite-like phase after the third cycle. This modification of the solid is reminiscent of that observed upon calcination. Here the solid is not carbonated, but the TGA experiment shows that dehydration starts at about 100 °C. The reaction temperature of 130 °C is then sufficient to provoke a significant dehydration, if we take into account that the reactor is swept by argon, and the reaction time relatively long. It can then be reasonably supposed that the dehydration of the catalyst surface is the cause of the decrease of catalytic activity.

4. Conclusions

In conclusion, we have developed an efficient method using heterogeneous catalysts to obtain glycerol carbonate and glycerol dicarbonate from glycerol. The experimental results show that the type of basic centre has a large influence on the activity in the heterogeneous glycolysis reaction. In addition, the absorption capacity of the Brønsted heterogeneous catalyst favours the subsequent transesterification of the glycerol carbonate. HTr4 was the best catalyst and could be recycled a few times. Thus it is concluded that Mg/Al mixed oxide catalysts and rehydrated catalysts are promising candidates for the transesterification reaction and would be able to replace homogeneous catalysts that have similar activity. It is however observed that the structure of the meixnerite active phase is lost after reaction, suggesting that the solid is dehydrated in the course of the reaction. This opens a path to a possible stabilization of catalytic activity.

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