Chemicals from biomass: Synthesis of glycerol carbonate by transesterification and carbonylation with urea with hydrotalcite catalysts. The role of acid–base pairs

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ABSTRACT

Synthesis of glycerol carbonate has been performed by transesterification of ethylene carbonate with glycerol catalyzed by basic oxides (MgO, and CaO), and mixed oxides (Al/Mg, Al/Li) derived from hydrotalcites. The results showed that the optimum catalyst in terms of activity and selectivity is a strong basic Al/Ca-mixed oxide (AlCaMO) which is able to catalyze the reaction at low temperature (35 °C), and low catalyst loading (0.5 wt%) giving high glycerol conversions with 98% selectivity to glycerol carbonate. When the synthesis of glycerol carbonate was carried out by carbonylation of glycerol with urea, the results showed that balanced bifunctional acid–base catalysts where the Lewis acid activates the carbonyl of the urea and the conjugated basic site activates the hydroxyl group of the glycerol were the most active and selective catalysts.

1. Introduction

Much interest has been developed in the last years for the use of renewable feedstocks [1] and fats and oils not competing with food can become very important players in the chemical industry for the near future. Their competitive cost, worldwide availability, and built-in functionality make them attractive for numerous commercial applications. One application is the production of biodiesel by transesterification processes with methanol or ethanol. The growing production of biodiesel has generated a surplus of glycerine and its price can be lower than that of propylene glycol or sorbitol.

Glycerol is a synthesis intermediate for the preparation of a large number of compounds via oxidation [2], etherification [3], esterification, transesterification [4], polymerisation, etc. Therefore, it is not surprising that a large effort has been devoted in the last years for converting glycerol into high value-added chemicals [5].

One important glycerol derivative is the glyceryl carbonate (GC) which is widely used as protic solvent (in resins and plastics) [6], additive, and as chemical intermediate. Due to its low toxicity, low evaporation rate, low flammability, and moisturizing ability, GC is used as wetting agent for cosmetics and carrier solvent for medical preparations.

On the other hand, the presence of a cyclic carbonate group along with a primary hydroxylmethyl group allows the molecule

to react with anhydrides [7] to form ester linkages or with isocyanates to form urethane linkages [8]. These materials are used for the production of polyurethane protecting coatings for wood and metal substrates. Besides, GC is the most valuable intermediate for the production of glycidol which is a precursor for the synthesis of polymers [9].

The main methods for the preparation of GC are based on the reaction of glycerol with (a) a carbonate source (phosgene, a dialkyl carbonate [10] or an alkylene carbonate), (b) urea, and (c) carbon monoxide and oxygen. Traditionally, cyclic carbonates have been prepared by reaction of glycols with phosgene, but due to the high toxicity and corrosive nature of phosgene alternative routes such as transesterification reaction of dialkyl or alkykene carbonates to obtain cyclic carbonates have been explored [11–15]. For instance, ethylene carbonate, a commercial product with interesting physical properties (low toxicity, low evaporation rate, biodegradability, high solvency, etc.) has been widely used as carbonate source for preparing GC. The transesterification between glycerol and ethylene carbonate (EC) to produce GC is performed with an alkaline base. For instance, using sodium bicarbonate, at 130 °C, the yield of glycerol carbonate reached 81% after 30 min [11]. However, the main problem associated with these catalysts is the requirement of a final neutralization step. For doing this, at the end of the reaction, a mineral acid (phosphoric acid, sulphuric acid, benzenesulphonic acid, etc.) is added to the system to neutralize the catalysts, followed by distillation under reduced pressure for the recovery of GC from the reaction mixture, which contains reactants, salts and products.

Despite the fact that heterogeneous base catalysts should allow easy separation and recycling of the catalyst by filtration avoiding the neutralization step and reducing waste formation, there are few examples for the synthesis of GC by transesterification of EC and glycerol in the presence of solid catalysts. Thus, Sugita et al. [12] have performed the transesterification reaction in the presence of aluminium oxide as catalyst. When the reaction was carried out at 135–140 °C under reduced pressure with progressive removal of ethylene glycol, GC is obtained with 99% yield.

More recently, a process for the preparation of GC by transesterification of ethylene carbonate with glycerol in the presence of an anionic bicarbonated or hydroxylated macroporous resin (Amberlyst A26) and basic form zeolites (Y, X, A), has been reported in the patent literature [13]. In this case, when the transesterification reaction was carried out in the presence of basic KX zeolite in a molar ratio ethylene carbonate/glycerol of 2, at 80 °C, 81% yield of GC was obtained after 2 h reaction time. When a reactor which allows the distillation of ethylene glycol formed was used 99% yield of GC was obtained.

The transcarbonation between ethylene carbonate and glycerol in supercritical CO_2 using zeolites or strongly basic resins has also been performed, though in this case the yields of GC were lower than 25% [14]. Concerning the preparation of GC from urea and glycerol, the same authors have patented a process for preparing GC using metallic or organometallic salts, or supported metallic compounds. The best results (GC yield 80%) were obtained using a calcined $ZnSO_4$ as catalyst with a molar ratio glycerol/urea of 1, at 150 °C and 40 mbar, while removing the ammonia formed during the reaction [15]. Okutsu and Kitsuki [16] have prepared GC by reacting glycerol with urea with a metal oxide such as ZnO in the presence of a dehydrating agent such as anhydrous $MgSO_4$. Thus a mixture of glycerol and anhydrous magnesium sulphate was heated at 120 °C in the presence of nitrogen. After 2 h, urea and zinc oxide were added. After 6 h reaction time, the conversion of glycerol was 62–65% with selectivity close to 92%. Better results have been recently reported by the same authors using $ZnSO_4$ as catalyst [17]. Performing the reaction at 130 °C, 90% yield of GC was obtained after 10 h reaction time. However, when the reaction was performed using $MgSO_4$ as a catalyst and in the presence of diethylene glycol diethyl ether as solvent only 58% yield of GC was obtained after 24 h reaction time [18].

Finally, GC has also been directly prepared by oxidative carbonylation of glycerol by reacting glycerol with a gaseous mixture of carbon monoxide and oxygen. Thus, Teles el al. [19] have described a process that uses salts of the elements of groups Ib, IIb, and VIIb (copper, silver, mercury, cobalt, etc.) as catalysts. More specifically, the reaction takes place in an inert solvent such as nitrobenzene at 130 °C, with a gas mixture of CO/O_2 (95:5%) at 8 bar in the presence of copper (I) chloride as catalyst. Under these reaction conditions and after 20 h, 96% yield of GC was obtained.

In this work we have studied the possibility of preparing prepare GC in high yields and selectivity using solid catalysts with adequate acid–base pairs. For doing this, we have chosen the reaction of transcarbonation of glycerol with ethylene carbonate and carbonylation of glycerol with urea.

2. Experimental

2.1. Materials

Glycerol (99.5%), ethylene carbonate, and urea were purchased from Aldrich and used without further purification. The ZnO and CaO commercial samples were purchased from Fluka. MgO was purchased from NanoScale Materials Inc. Sn-Beta zeolite was synthesized according to the literature procedures [20].

The Al/Mg hydrotalcite was prepared by co-precipitation at constant pH and controlled by slow addition in a single container of two diluted dilutions (A and B), namely, solution A containing $Mg(NO_3)_2$ and $Al(NO_3)_3$, 1.5 M in Al + Mg with Al/Al + Mg atomic ratio equal to 0.25, and solution B prepared by dissolving Na_2CO_3 and NaOH in water in such way that the ratio $CO_3^{2-}/(Al + Mg)$ is equal to 0.66.

In order to prepare an Al/Ca hydrotalcite, the same methodology was followed using $Ca(NO_3)_2$ as solution A in this case.

The Al/Zn/Li hydrotalcite was prepared following the same methodology using $Al(NO_3)_3$, $Zn(NO_3)_2$ (1.5 M in Al + Zn) + LiCl (5 mol% respect to Al + Zn) with Al/(Al + Zn + Li) atomic ratio equal to 0.25, as solution A.

The Al/Mg/Fe hydrotalcite was prepared following the same methodology using $Al(NO_3)_3$, $Mg(NO_3)_2$ and $Fe(NO_3)_3$ (Fe = 5 mol% respect to Mg + Fe), solution 1.5 M in Al + Mg + Fe, with Al/(Al + Mg + Fe) atomic ratio equal to 0.33 as solution A.

In all cases, the solutions A and B were mixed at 60 mLh^{-1} addition rate, for 4 h, with vigorous stirring. The final pH was of 13. The co-addition process was carried out at room temperature. The sample was aged at 60 °C for 24 h. Finally, the precipitate was filtered and washed to eliminate the alkali metals and the nitrate ions until the pH of the washing water was 7 and then dried at 60 °C for 12 h.

The Al/Li layered double-hydroxyl carbonate ($[Al_2Li(OH)_6]_2$-$CO_3 nH_2O$) with a Al/(Al + Li) molar ratio of 0.33 was prepared by adding a hexane solution of aluminium-tri-(sec-butoxide) (17 wt/wt%) to a lithium carbonate aqueous solution (0.55 wt/wt%) under vigorous mechanical stirring at room temperature. The suspension was left for 24 h at 60 °C. The Al/Li hydrotalcite was filtered and washed until pH 7 and the solid was dried at 60 °C.

The Al/Zn hydrotalcite was synthesized by mixing an aqueous solution of zinc nitrate hexahydrate and aluminium nitrate nonahydrate with a basic aqueous solution containing sodium hydroxide and sodium nitrate. The molar ratios of the reagents $Zn(NO_3)_2 6H_2O/Al(NO_3)_2 9H_2O/NaNO_3/NaOH$ were 2.1:0.9:4:4.9. The metal and the basic solutions were added together at a rate of 1 mL/min under vigorous stirring. The resulting gel of pH 5.84 was aged at 60 °C for 18 h. The hydrotalcite formed was dried at 100 °C overnight.

The different hydrotalcite-like materials synthesized were analyzed by X-ray diffraction (XRD) with a Phillips PW diffractometer using Cu Kα radiation. Fig. 1 shows the XRD patterns of the different hydrotalcite-like materials. As can be observed HTAl-Mg, HTAl-Mg-Fe, and HTAl-Li showed the characteristic peaks corresponding
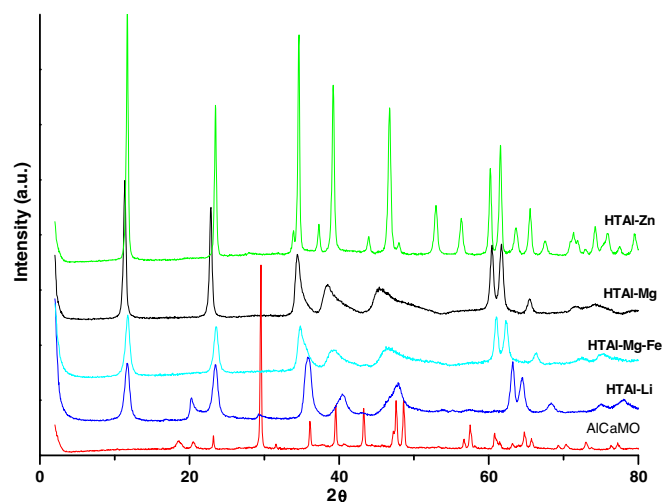

Fig. 1. XRD patterns of the different basic catalysts.

to well-crystallized hydrotalcite structure. In the case of HTAl-Zn, besides the characteristics peaks of hydrotalcite phase, some impurities corresponding possibly to Zn carbonates and oxyhydroxycarbonates are also observed. On the other hand, the XRD pattern of the Al/Ca material showed that it does not correspond to a hydrotalcite structure, but to a mixture of CO_3Ca and $Al(OH)_3$ phases.

For its use as basic catalysts, hydrotalcites were calcined at 450 °C for 6 h in a nitrogen flow in order to obtain the corresponding mixed oxides and denoted as HTc-Mg, HTc-Li, HTc-Zn, HTc-Zn-Li, and HTc-Fe. The mixture of CO_3Ca and $Al(OH)_3$ was calcined at 450 °C for 6 h in a nitrogen flow and labeled as AlCaMO (Al/Ca-mixed oxide).

In the case of Al/Mg hydrotalcite, the resulting mixed oxide was hydrated at room temperature by adding directly 36 wt% of decarbonated water (MilliQ) just before the use and is denoted as HTr.

For the screening of catalytic activity all the catalysts have just been calcined before their use.

The materials synthesized were analyzed by Inductively Coupled Plasma (ICP) using a Varian 715-ES ICP Optical Emission Spectrometer and by X-ray diffraction (XRD) with a Phillips PW diffractometer using Cu Kα radiation. Specific surface areas of the different materials were obtained with an ASAP 2000 (Micromeritics) using the BET methodology. The main characteristics of solid catalysts are summarized in Table 1.

2.2. Reaction procedure: transcarbonation of ethylene glycol carbonate with glycerol

The experiments were performed in a glass batch reactor equipped with a condenser system. The catalyst was calcined just before its use at 450 °C and added to the reactor at the same time that reactants. The system of reaction was stirred and heated in a silicone bath to the required temperature in the absence of solvent, under nitrogen atmosphere. Samples were periodically taken out of the reactor and separated from the catalyst by filtration and analysed by gas chromatography. The gas chromatograph (Varian 3900) was equipped with a Trocar TR-WAX column (15 m × 0.32 mm × 0.25 m) and a flame ionization detector. After the completion of the reaction, the reaction mixture was filtered and the catalyst washed with acetone to wash off the products adhered on the surface of the catalyst. The combined filtrate fractions were concentrated under reduced pressure and the products were identified by GC–MS. Nitrobenzene was used as internal standard, and the conversion, selectivity and yield were calculated with respect to the limiting reactant.

2.3. Carbonylation of glycerol with urea

The reactions were performed in a 10 mL round-bottom flask with a side arm and a 90° angle adapter to connect it to a vacuum line. In a typical experiment glycerol was placed under reaction conditions for 10 min before urea and catalyst were added. The amount of catalyst used was always 5% by weight of the initial amount of glycerol. The reaction was stirred at a constant rate of 300 rpm, and heated in an oil bath at the desired temperature. Reactions were run under a reduced pressure and in the absence of a solvent. After the reaction was completed, methanol was added and the catalyst removed by filtration. The catalyst was washed with acetone to remove the adsorbed products. The filtrate fractions were concentrated under reduced pressure and the products were identified by GC–MS. Product quantification was made by using the response factor of the different compounds and tetraethylene glycol (TEG) as external standard. Conversion, selectivity, and yield were calculated with respect to glycerol.

The samples were analyzed with a Varian 3900 gas chromatograph equipped with a TR-WAX column (15 m × 0.32 mm × 0.25 μm) and flame ionization detector.

GC–MS measurements were made with an Agilent 6890N Network GC System equipped with a Tracer TR-WAX column coupled to an Agilent 5973 Network Mass Selective Detector.

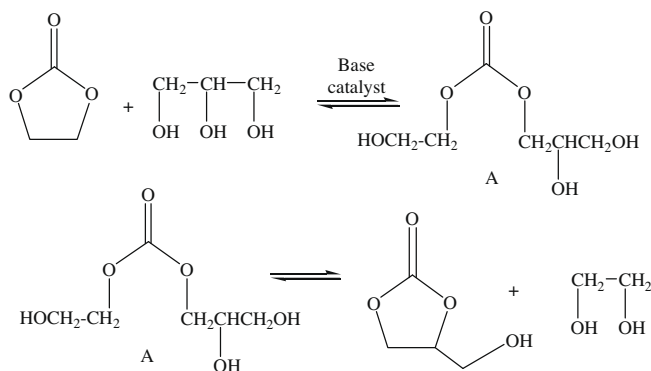### 2.4. Characterization: FTIR spectroscopy

Transmission FTIR spectra were recorded on a BioRad FTS-40A spectrometer. The samples were pressed into self-supporting wafers and placed in a stainless steel cell for low temperature experiments (CO adsorption at −175 °C) and in a quartz cell for room temperature experiments ($CHCl_3$ adsorption at 25 °C). Prior to the adsorption experiments the samples were activated in situ in a nitrogen flow at 450 °C for 3 h followed by evacuation at the same temperature at 10^{-5} mbar. CO adsorption experiments were done at −175 °C increasing the CO partial pressure (0.2–45 mbar). After CO saturation at −175 °C, the samples were evacuated and the spectra were collected at increasing temperature (−175 °C to −130 °C) under dynamic vacuum conditions. $CHCl_3$ adsorption experiments were done at 25 °C increasing the $CHCl_3$ partial pressure (1–23 mbar). The spectra were treated and deconvoluted using an Origin software.

2.5. XPS spectroscopy

XPS spectra were recorded on a SPECS spectrometer equipped with a Phoibos 150 9MCD detector using a non-monochromatic X-ray source (Al and Mg) operating at 200 W. The samples were pressed into a small disc and evacuated in the prechamber of the spectrometer at 1×10^{-9} mbar. Some of the samples have been activated in situ in nitrogen flow at 450 °C for 3 h followed by evacuation at 10^{-8} mbar. The measured intensity ratios of components were obtained from the area of the corresponding peaks after nonlinear Shirley-type background subtraction and corrected by the transmission function of the spectrometer. Casa software has been used for quantification and spectra treatment. Binding energy (BE) of the peaks have been corrected by charging effect according to Table 7.

3. Results and discussion

The catalytic transesterification of a cyclic carbonate with an alcohol involves two equilibrium steps, which typically generate a hydroxyl alkyl carbonate (compound A, Scheme 1) as reaction intermediate. Addition of a second molecule of alcohol (in this case the secondary hydroxyl group of the glycerol) of the intermediate product (A) results in the formation of the glycerol carbonate (4-hydroxymethyl-1,3-dioxolan-2-one) and ethyleneglycol. These two equilibrium reaction steps are presented in Scheme 1.

Table 1
Main characteristics of solid catalysts.

Catalyst	BET area ($m^2\,g^{-1}$)	Pore volume ($cc\,g^{-1}$)	Al/Al + M Molar ratio
HTc-Mg0.20	199	0.604	0.20
HTc-Mg0.25	265	0.625	0.25
HTc-Mg0.33	275	0.558	0.33
HTc-Li	240	0.657	0.33
AlCaMO	50	0.119	0.25
MgO	640	0.664	–
CaO	12	0.086	–
HTc-Zn	37	0.163	0.30
HTc-Fe	306	1.068	0.33
ZnO	5	0.090	–
HTc-Zn–Li	37	0.337	0.25

Scheme 1.

Fig. 2. Kinetics curves of transesterification between ethylene carbonate and glycerol in the presence of HTc-Mg ($\square$), MgO ($\circ$) and rehydrated hydrotalcite ($\bullet$).
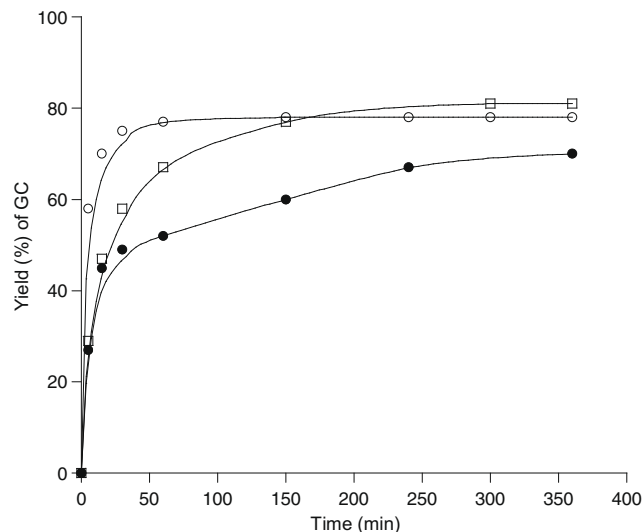
Recently we have shown that transesterification of fatty acid methyl esters with glycerol [4] and with polyethyleneglycol can be performed efficiently in the presence of solid basic catalysts such as MgO and mixed oxides [21]. Magnesium oxide with high surface area offers strong Lewis type-base sites (O^{2-}) associated with $Mg^2 + O^{2-}$ ion pairs in were the basic strength will depend on their coordination number. When aluminum is introduced into de brucite layer of MgO, hydrotalcites are formed. The hydrotalcites are layered double hydroxides (LDHs) which have the general molecular formula $M_x^2 + M_y^3 + (OH)_2(x+y)A_{y/n}^{-n}mH_2O$, where M^{2+} and M^{3+} are a divalent and a trivalent metal ions, respectively, and A^{-n} is an intercalated anion. Structurally, they possess brucite-like ($Mg(OH)_2$) sheets where isomorphous substitution of Mg^{2+} by a trivalent cation like Al^{3+} occurs. The resulting excess of positive charge in the layered network is compensated by anions, which occupy the interlayer space along with water molecules. By controlled thermal decomposition, LDHs are converted into mixed oxides (HTc) with high specific surface areas and strong Lewis basic sites.

Taking into account our previous results and considering that the transcarbonation is a transesterification type reaction, we have selected a high surface area MgO and an Al/Mg-mixed oxide derived from hydrotalcite with an Al/(Al + Mg) molar ratio of 0.25 (HTc-Mg0.25) as basic catalyst.

The reactions were performed in the absence of solvent, under inert atmosphere with an EC/glycerol molar ratio of 2, at 50 °C and using 7 wt% of catalyst. The results obtained are summarized in Table 2. In a preliminary experiment it has been observed that the transesterification is a slow reaction in the absence of catalyst, giving 5% yield of GC after 5 h of reaction time.

The HTc-Mg and MgO are the most active catalysts for the transesterification reaction. These results are consistent with the observation that these materials have basic sites strong enough for proton abstraction in cases where the pK_a of the hydrogen is close to 16, as it is the case of glycerol with a pK_a of 14 (measured in water at 25 °C) [22].

As can be seen, MgO with a high concentration of basic sites performs the transesterification at higher initial reaction rate than the HTc-Mg (Fig. 2). However the HTc-Mg catalyst is more selective than MgO which also forms glycidol as a reaction product.

It has been presented that the catalytic activity of calcined hydrotalcites can be increased by CO_2-free hydration at room temperature [23]. This treatment results in the restoration of the original layered structure, with OH^- as the compensating anions in the interlayer, which can act as Brönsted basic sites. It has been reported that the amount of water added on the calcined hydrotalcite has a strong influence on the catalytic activity because an excess of water on the catalyst surface can poison the basic sites decreasing catalytic activity [24]. In the reaction studied here, an optimum in catalytic activity was found with samples with 36 wt% water content. The result obtained for the transesterification reaction using HTr is summarized in Table 2 and Fig. 2. As can be seen in Fig. 2 initial rates of formation of GC are similar for HTr and HTc-Mg catalysts, indicating that in this case Brönsted and Lewis basic sites possess similar activity. However, the final conversion of glycerol and selectivity to GC on the HTr hydrotalcite is lower than in the case of HTc-Mg. As can be observed in Fig. 2, HTr exhibits a higher deactivation rate than HTc-Mg, which can be related to a stronger adsorption of the highly polar reactants and products involved in the reaction that may block the active sites. On the other hand, glycidol is formed in higher amounts in the hydrated than in the non-hydrated sample lowering, therefore, the final selectivity.

According with the results presented in Table 2, it appears that mixed oxides can be suitable catalysts in terms of activity and selectivity for the transesterification of EC and glycerol to produce GC. Therefore it is of interest to improve the activity of the mixed oxide to operate at lower temperature and reaction times since cyclic carbonates are heat-sensitive, and prolonged reaction times can promote decomposition of cyclic carbonates (EC and GC).

Table 2
Results of transesterification between EG and glycerol on different heterogeneous base catalysts.

Catalyst	Conversion glycerol (%)	Yield GC (%)	Yield glycidol (%)	Intermediate A (%)	Selectivity GC (%)
–	20	5	–	15	43
HTc-Mg0.25	85	82	<1	2	96
MgO	86	78	3	5	90
HTr	78	68	7	3	87

Reaction conditions: 16 mmol EC, 8 mmol glycerol, 7 wt% of catalyst respect to the total weight of reactants, at 50 °C, 5 h reaction time.

3.1. Influence of chemical composition

It is known that by increasing the aluminum content in an Al_2O_3–MgO mixed oxide (HTc-Mg) the basic site density decreases, while the fraction of the strong basic sites increases [25]. Therefore and in order to improve the activity of mixed oxides for the transesterification reaction three samples with Al/Al + Mg molar ratios of 0.20, 0.25, and 0.33 have been prepared. The results obtained for the transesterification reaction with the above samples are given in Fig. 3. As can be observed, HTc-Mg with Al/(Al + Mg) molar ratios of 0.20 and 0.25 shown similar activity, whereas the sample with Al/(Al + Mg) molar ratio of 0.33 shows lower activity. These results indicate that in the samples prepared, the introduction of stronger basic sites does not compensate the decrease in the number of active sites produced by increasing the Al^{3+} content.

A further increase in basicity can be achieved by replacing Mg^{2+} by more electropositive ions such as Li^+ and Ca^{2+} [4]. By doing this, the density of negative charge on the oxygen increases, leading to an increase of the basicity of the resulting mixed oxide. To check the effect of this modification on catalyst activity, an HTc-Li sample with an Al/Al + Li = 0.33 was synthesized. However, when we try to synthesize an HTc-Ca sample with an Al/Al + Ca = 0.25 as described in the experimental section, according to XRD analysis, a mixture of $CaCO_3 + Al(OH)_3$ was obtained. This material was calcined (AlCa-MO) and tested as basic catalyst in the transesterification reaction.

The transesterification of ethylene carbonate with glycerol was tested using these samples as catalyst under the same reaction conditions than above, and their activity resulted much higher when compared with the Al/Mg-mixed oxide, in such way that temperature and amount of catalyst were strongly lowered being possible to operate at 35 °C and 0.5 wt%, respectively. The results obtained are presented in Table 3, where it can be observed that
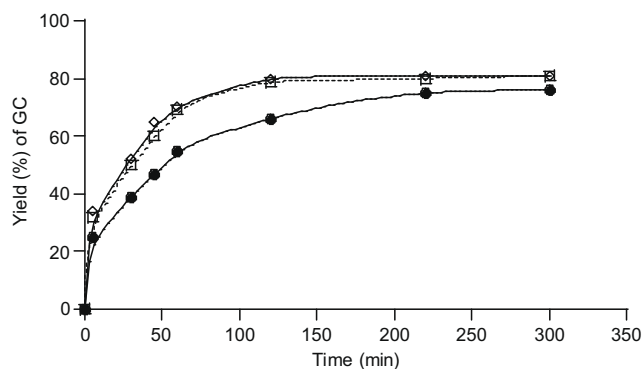
the presence of stronger Lewis basic sites results to be very beneficial and the catalysts perform the transesterification reaction more efficiently than with HTc-Mg, the selectivity in all cases being very high. Interestingly glycidol was not detected in the reaction media, the selectivity to GC being above 96%.

For comparative purposes, the reaction was also performed with CaO as basic catalyst, and as occurred with MgO, the activity for converting glycerol was very high, but the selectivity to GC was lower due to the formation of glycidol.

From the results presented we can conclude that a correlation does exist between the catalytic activity and the basic properties of the catalyst for transesterification reaction. This correlation between basic properties of solid catalysts and catalytic activity has been observed by Figueras et al. [26] in the transcarbonation of 1-phenyletanol with diethylcarbonate in presence of CsF, KF supported on alumina and Mg/La mixed oxide. In our case the presence of stronger Lewis basic sites in the HTc-Li and AlCaMO catalysts allows to carry out the reaction under very mild reaction conditions and short reaction times, with excellent selectivities and yields.

3.2. Catalysis deactivation

To study catalyst deactivation HTc-Mg, HTc-Li and AlCaMO were reused several times under the same reaction conditions. Thus, after completion of the transcarbonatation reaction the solid was filtered, washed with methanol (5×2.5 mL) and acetone to remove the products adhering to the surface of the catalysts, dried at room temperature and reused. As can be seen in the Table 4 the conversion slightly decreased while selectivity was maintained after three catalytic cycles when using HTc-Mg and HTc-Li. On the other hand, when using AlCaMO some deactivation is observed after 1 h reaction time.

From these results obtained we can conclude that with HTc-Li and AlCaMO catalysts, excellent yield and selectivity to GC can be obtained under very mild reaction conditions. Moreover the catalysts can be recycled, and activity is basically maintained.

Fig. 3. Influence of chemical composition of Al/Mg mixed oxides in the transesterification between glycerol and ethylene carbonate using HTc-Mg with Al/Al + Mg ratio of 0.20 (◇), 0.25 (□), and 0.33 (●).

Table 4
Results of the reuse of the mixed oxides in the transesterification of EC and glycerol.

Catalysts	Conversion (selectivity to GC)			
	t (h)	1st cycle	2nd cycle	3rd cycle
HTc-Mg0.25	1	57(98)	57(98)	47(97)
HTc-Li	1	88(96)	88(97)	86(96)
AlCaMO	1	89(98)	74(98)	72(98)
	4	92(97)	90(96)	90(96)

Reaction conditions: 24 mmol ethylene carbonate, 12 mmol de glycerol, 0.5 wt% of catalyst respect to the total weight of reactants at 35 °C.

Table 3
Catalytic performance of HTc-Li, AlCaMO, CaO and HTc-Fe for the synthesis of GC.

Catalyst	t (min)	Glycerol conversion (%)	Yield GC (%)	Yield glycidol (%)	Yield of intermediate A (%)	Selectivity GC (%)
HTc-Li	15	83	81	0	2	97
	60	88	85	0	3	96
AlCaMO	15	87	85	0	3	98
	60	89	87	0	2	98
CaO	15	90	81	5	4	90
	60	92	83	6	3	90
HTc-Fe	15	80	65	10	5	81
	60	84	70	10	4	83

Reaction conditions: 24 mmol ethylene carbonate, 12 mmol glycerol, 0.5 wt% of catalyst with respect to the total weight of reactants at 35 °C.

3.3. Preparation of glyceryl carbonate from urea and glycerol

Another interesting route of producing glyceryl carbonate is the reaction between glycerol and urea. The main advantage of this method is that urea is the readily available and cheap reactant. In addition, ammonia formed can be easily converted to urea since the urea synthesis is performed from ammonia and carbon dioxide.

The accepted mechanism for the reaction of urea with alcohols involves two steps [27] and that in the specific case of glycerol it will be as follows: first the carbamoylation of glycerol to glycerol carbamate liberating a mol of ammonia. This step occurs at higher reaction rate than the second step, the carbonylation of the glycerol urethane to glycerol carbonate with elimination of a second mol of ammonia (Scheme 2).

As described above, the reaction between urea and glycerol has been performed using $ZnSO_4$ and ZnO catalysts. High yields are reported using $ZnSO_4$ as catalyst [15,17,28], however, this salt is soluble in glycerol and the reaction takes place under homogeneous catalysis with the catalysts being partially recovered after the reaction.

Ball et al. [27] reported that the reaction between primary and secondary alcohols with urea to form alkyl carbonates can be improved using an adequate combination of a weak Lewis acid and a Lewis base. More recently Li et al. [29] reported that catalysts exhibiting adequate acid and base properties were favorable to the synthesis of cyclic carbonates from urea and diols. The authors claim that the presence of Lewis acid sites able to activate the urea is an important feature of the catalyst to achieve high yields of the cyclic carbonate, and ZnO appeared to be the optimum catalyst. It should be remarked however that with ZnO high ratios of urea glycerol (up to 4 mol mol^{-1}) are normally used.

Taking into account all the above-mentioned features, a mechanism can be proposed that involves Lewis acid site able to activate the carbonyl group, that will be now more prone to the nucleophilic attack of the glycerol adsorbed on the Lewis basic site (Scheme 3).

In order to find solid and recyclable heterogeneous catalysts able to perform efficiently the reaction between the urea and glycerol we have prepared a series of solid materials with different acid–base properties. The reactions were performed under reduced pressure in order to shift the thermodynamic equilibrium by removing the ammonia formed. Reaction conditions (temperature, amount of catalyst, pressure and molar ratio and reaction time) were optimized using ZnO that was taken as reference. We have selected as optimized parameters: 5 wt% of catalyst with respects to glycerol, 145 °C reaction temperature, 30 Torr of pressure, glycerol to urea molar ratio of one and 5 h reaction time. The results obtained are summarized in Table 5.
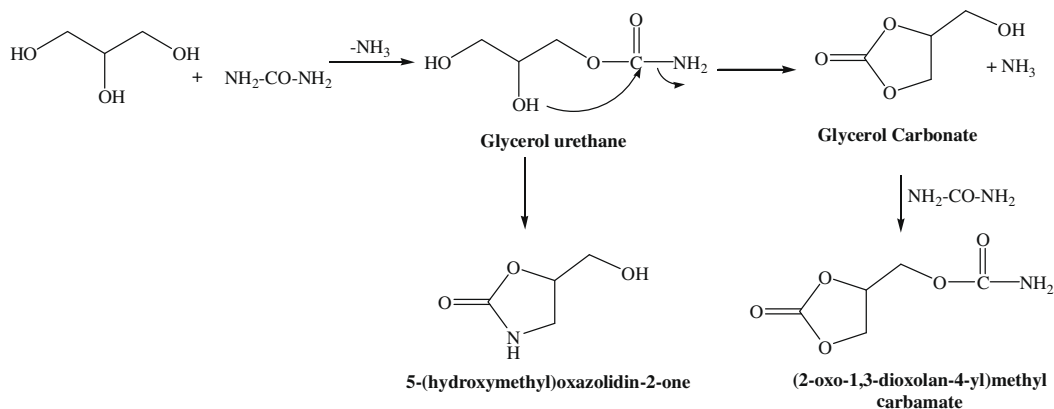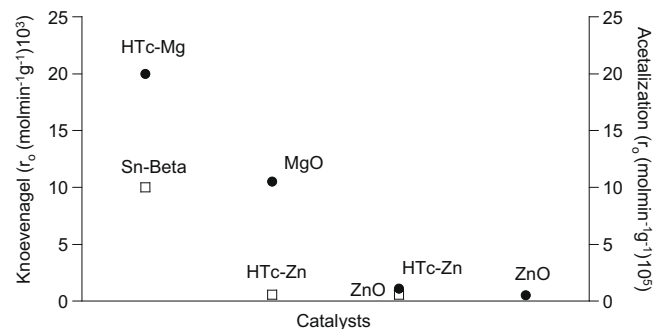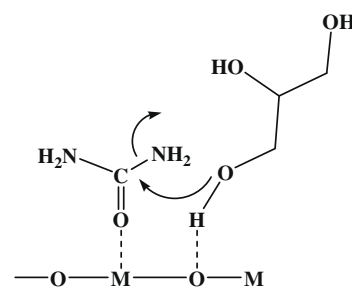

Fig. 4. Results of the Knoevenagel condensation between benzaldehyde (10 mmol) and malononitrile (10 mmol) 5 wt% of catalyst at room temperature (●), and acetalization of benzaldehyde (5 mmol) with TMOF (25 mmol) 5 wt% of catalyst in CCl_4 (8 mL) at 76 °C (□).

Scheme 3.

3.4. Catalyst characterisation: acid–base properties

The relative acidity and basicity of various representative solid catalysts of this series, was determined by two test reactions: the Knoevenagel condensation between malononitrile and benzaldehyde which is typically catalyzed by bases, and the acetalization of benzaldehyde with trimethylorthoformate (TMOF), which is a reaction catalyzed by purely acid sites. Results of initial rates for Knoevenagel condensation and acetalization for the catalysts with different acid–base pairs are presented in Fig. 4. As can be observed the order of activity for the Knoevenagel condensation which can be associated with the order of catalysts basicity is: HTc-Mg0.25 > MgO > HTc-Zn > ZnO. On the other hand, the order of activity for the acetalization reaction which can be associated with the order of catalysts acidity is: Sn-Beta > HTc-Zn ≈ ZnO, while HTc-Mg and MgO gave negligible activity.

Scheme 2.

Table 5
Results of carbonylation of glycerol and urea in the presence of different solid catalysts.

Entry	Catalyst	Glycerol conversion (%)	GC yield (%)	GC selectivity (%)
0	Without	25	15	60
1	Beta-Sn	70	26	37
2	MgO	73	39	53
3	HTc-Mg0.25	93	5	5
4	AlCaMO	80	10	12
5	ZnO[a]	80	60	75
6	HTc-Zn[b]	82	72	88
7	HTc-Zn/Li	84	27	32
8	HTc-Fe/Mg	78	39	50

Reaction conditions: Glycerol/urea molar ratio = 1, 30 Torr, 145 °C, 5 wt% catalyst at 5 h of reaction time.
  [a] 2% glycerol carbamate, 4% (2-oxo-1,3-dioxolan-4-yl)methyl carbamate, and 3% of 5-(hydroxymethyl)oxazolidin-2-one and 3% unidentified products and traces of glycidol were detected.
 [b] 2% glycerol carbamate, 3% (2-oxo-1,3-dioxolan-4-yl)methyl carbamate, 1% of 5-(hydroxymethyl)oxazolidin-2-one and 3% of unidentified products, and traces of glycidol were detected.

Catalysts acidity and basicity has been also evaluated by FTIR spectroscopy of adsorbed probe molecules: CO for surface acidity and chloroform for surface basicity. Fig. 5 shows the IR spectra of CO adsorbed at −170 °C at increasing equilibrium pressure on MgO, HTc-Zn and Sn-Beta catalysts. CO interaction with coordinatively unsaturated surface sites causes a shift of the C–O stretching vibration to higher frequencies from that of the free molecule (2143 cm^{-1}). This shift is associated to the Lewis acidity of the surface site. Indeed a correlation between the electric field strength at the surface site and the CO frequency shift has been proposed [30]. The IR spectra of CO adsorbed on MgO shows one band at 2155 cm^{-1} together with a shoulder at 2166 cm^{-1} associated to two different types of Mg^{2+} surface sites [31] and an IR band at 2145 cm^{-1} associated to physisorbed CO. On Sn-Beta sample CO adsorption leads to IR bands at 2189 (weak, which becomes resolved at low CO coverages, see Fig. 5), 2177 and 2156 cm^{-1} associated to different co-ordinated Sn^{4+} surface sites [32], an IR band at 2141 cm^{-1} associated to OH groups according to the simultaneous shift of the hydroxyl groups, and an IR band at 2133 cm^{-1} due to physisorbed CO. On HTc-Zn IR bands at 2204, 2187 and 2175 cm^{-1} associated to CO interacting with Al^{3+} and Zn^{2+} Lewis surface sites [33] are observed and an IR band at 2152 cm^{-1} due to OH groups and an IR band 2132 cm^{-1} due to physisorbed CO. Assignation of the IR band at 2152 cm^{-1} to OH groups is supported by the simultaneous shift of the hydroxyl groups. However the contribution of some weak Lewis acid sites to the 2152 cm^{-1} IR band cannot be completely ruled out. Thus, from the IR spectra of CO adsorption and the shift in the CO-stretching vibration of the adsorbed CO molecules, a higher Lewis acidity of surface sites on HTc-Zn and Sn-Beta samples than on MgO sample can be inferred. On the other hand, while both Sn-Beta and HTc-Zn samples show similar shift in the CO-stretching vibration of adsorbed CO molecules (IR bands at 2189, 2173, and 2154 cm^{-1}), the higher thermal stability of the IR bands in the Sn-Beta sample point to a slight higher acid strength on this sample compared to the HTc-Zn sample (Fig. 6). Moreover, Sn-Beta sample shows a higher amount of Lewis acid surface sites than HTc-Zn sample (1.568 Lewis sites, a.u./mgr, in Sn Beta and 0.047 Lewis sites, a.u./mg, in HTc-Zn). According to this results, the higher acidity observed on Sn-Beta sample versus HTc-Zn in the acetalization of benzaldehyde used as test reaction for order of acidity cannot only be related to the slight difference in acid strength between both samples but mainly to the higher amount of Lewis acid sites in the Sn-Beta sample.
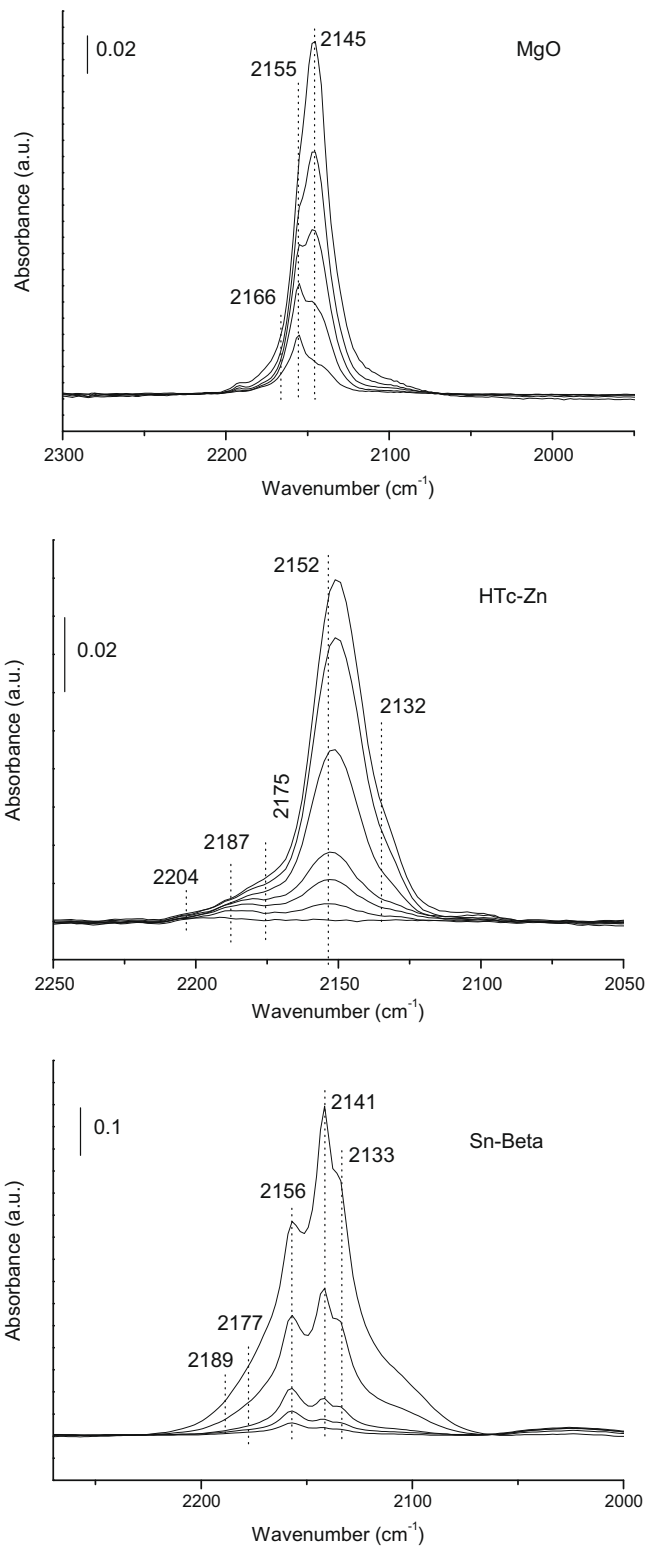

Fig. 5. FTIR spectra of CO adsorption at −170 °C on MgO, HTc-Zn and Sn-Beta samples at increasing CO equilibrium pressure.

Fig. 7 shows the IR spectra of chloroform adsorbed at 25 °C at increasing partial pressure on MgO, HTc-Zn and Sn-Beta samples. Chloroform has been used as probe molecule for studding the basicity of the samples. The high basicity of MgO lead to a partial decomposition of chloroform giving formiat species (IR bands at 2846 and 1600 cm^{-1}). On the other hand, the IR bands at 3020
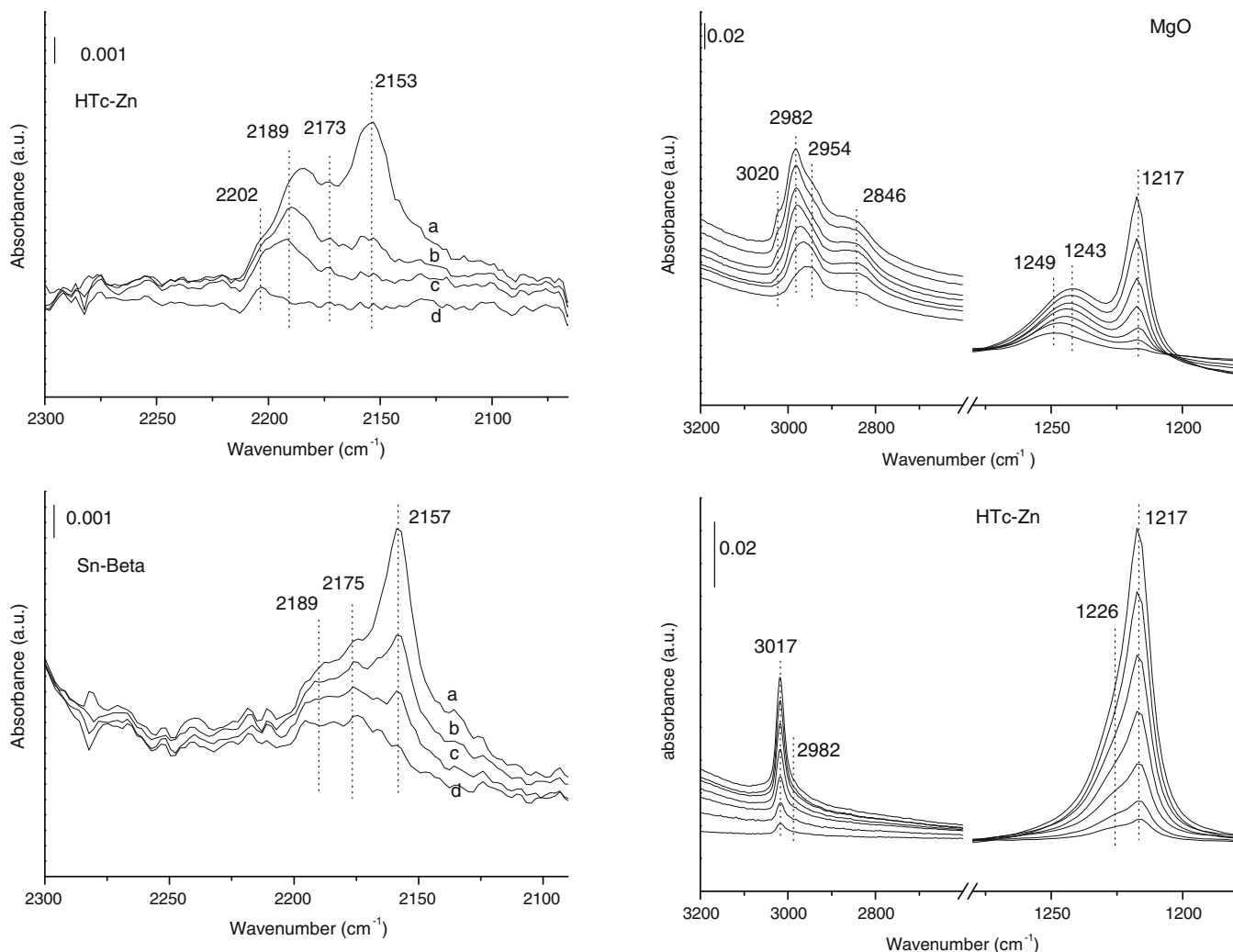
Fig. 6. FTIR spectra of CO adsorbed on MgO and HTc-Zn samples at increasing temperatures (a) −170 °C, (b) −160 °C, (c) −153 °C, (d) −132 °C under dynamic vacuum conditions.

and 1217 cm^{-1} associated to the ν(C–H) stretching vibration and the ν(HCCl) deformation mode, respectively, are close to those observed on liquid CHCl$_3$ and associated to chloroform interacting with the OH groups of the MgO surface (Cl–HO interaction) according to the simultaneous shift of the hydroxyl groups. In addition, the IR bands at 2982, 2954 cm^{-1} and 1243, 1249 cm^{-1} can be associated to chloroform interacting with Lewis basic sites of the MgO surface. Different modes of interaction of CHCl$_3$ in which acid–base pairs or only base sites are involved could explain the presence of the two IR bands [34]. On the HTc-Zn sample formiat species are not observed in agreement to a lower basicity. On the other hand, IR bands at 3017 and 1217 cm^{-1} corresponding to CHCl$_3$ interacting with OH groups are observed together with another bands at 2982 and 1226 cm^{-1} associated to chloroform interacting with surface base sites. The lower shift of these bands compared to those observed on MgO points to a lower basicity of the sample. On the other hand on Sn-Beta only bands due to CHCl$_3$ interacting with OH groups are observed (IR band at 3019 cm^{-1}). The ν(HCCl) deformation vibration is hidden due to the strong framework adsorption. Thus form the IR spectra of CHCl$_3$ adsorption we can conclude that the basicity of MgO is higher than HTc-Zn and both of them higher than Sn-Beta sample, which agree with the order of activity observed in the Knoevenagel condensation reaction.
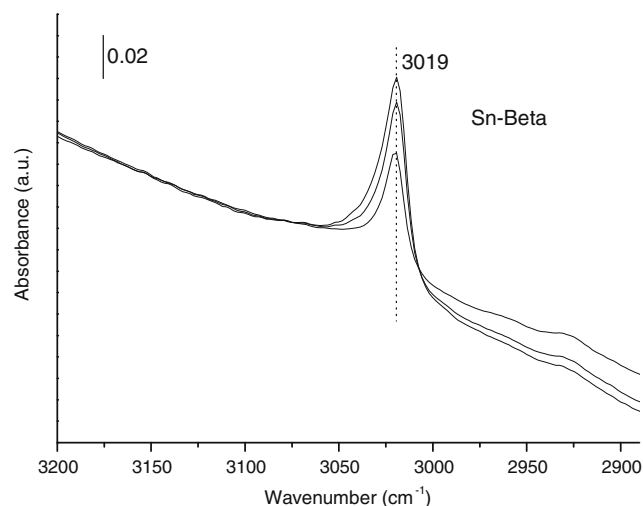
Fig. 7. FTIR spectra of CHCl$_3$ adsorbed at 25 °C on MgO, HTc-Zn and Sn-Beta samples at increasing equilibrium pressure.

3.5. Catalyst performance in the carbamoylation between urea and glycerol

When the carbamoylation reaction between urea and glycerol was performed in the presence of a material with strong Lewis acid sites associated to a very weak conjugated base pair, such as that in

the case of Sn-Beta zeolite, low glycerol conversion and low selectivity to GC were observed (entry 1 in Table 5). Increasing the base strength using MgO or MgO–Al$_2$O$_3$-mixed oxide derived from hydrotalcites (entries 2 and 3 in Table 5), high conversions of glycerol with very low selectivities to GC are obtained. In both cases, polymerization of glycerol carbonate and/or glycerol into heavy polymers is highly favored with the main responsible for the low selectivity to glycerol carbonate observed.

Using a ZnO catalyst (entry 5) which has a lower basic strength and higher acidity of the conjugated acid than MgO or Al/Mg-mixed oxides, activity and selectivity were improved, in agreement with the previous reports [35,29]. However, we have found that when the strength of the Lewis acid sites (Zn) was maintained and the basic site strength of the conjugated base was increased by preparing an Al/Zn-mixed oxide (entry 6), activity and selectivity were the highest. Thus, the most active and selective catalyst HTc(Al/Zn) gives 82% conversion of glycerol with 88% selectivity to GC. In addition low amounts of the intermediate glycerol carbamate (2,3-dihydroxypropyl carbamate), 5-(hydroxymethyl)oxazolidin-2-one, and (2-oxo-1,3-dioxolan-4-yl)methyl carbamate (Scheme 2), besides negligible amount of unidentified by-products were also detected working with an urea to glycerol ratio of 1 mol mol^{-1}.

The excellent performance of this catalyst can be attributed to the existence of well balanced acid–basic properties. Thus whereas strong Lewis acid or basic sites promote mainly polymerization reactions, a cooperative effect between weak metal Lewis acid sites able to activate the carbonyl group of the urea, and Lewis basic sites able to activate the glycerol, could be the responsible for the high catalytic performance observed with Al/Zn oxides. If on the contrary we increase the basicity of the hydrotalcite by introducing Li, while maintaining the ZnO, the yield strongly decreases.

3.6. Deactivation of the Al/Zn mixed oxide

To evaluate catalyst deactivation and recycling, the Al/Zn mixed oxide was rinsed after the first use (entry 1, Table 6), with methanol, air-dried, and used again under exactly the same conditions (entry 2). A 9% decrease in selectivity occurred. This process was repeated with the same material and conditions in entry 3, which gave similar selectivity than in the second cycle. The catalyst was then extracted with methanol in a soxhlet setup, and used again (entry 4) giving similar yield. Finally, the catalyst was calcined after four reuses, and the catalytic results with the calcined sample shows a slightly lower yield (entry 5) to the previous reactions. In other words catalyst deactivation results show that there is a decrease in yield after the first reuse, but after this its activity remains constant in further reuses.

3.7. Surface characterisation of fresh and re-used catalysts

Surface characterisation of three selected samples has been done by XPS and shown in Table 7. The samples have been analysed after "in situ" activation (450 °C 3 h in nitrogen flow) and after reaction. XPS data of "used" samples shows an increase in the amount of carbon (C1s) due to adsorbed surface species and some structural changes in the composition and chemical nature of surface sites. In fact, a lower BE of Zn2p and Al2p XPS peaks and the presence of two components related to aluminium species in different environment are observed in the HTc-Zn sample after reaction. Moreover an apparent increase in the Al/Zn ratio is observed after reaction. However the lower ineslatic mean free path of Zn2p electrons (0.49) versus Al2p electrons (1.124) and the presence of several layers of adsorbed surface species could contribute to the increase in the Al/Zn ratio. On the other hand, in the Sn-Beta sample a lower BE of Sn3d XPS peak is observed together with a decrease in the Sn/Si ratio. The ineslatic mean free paths of Sn3d electrons (0.87) and Si2p electrons (1.01) are quite similar, thus the decrease in the Sn/Si ratio should be due to some structural factors. In the same way in MgO sample a lower BE of Mg2s XPS peak is observed in the sample after reaction. The decrease in the BE of Zn2p, Al2p, Sn3d, and Mg2s on the samples after reaction can be related to a change in the electronic charge of the surface site, either due to the presence of adsorbed species or due to some structural modification of the samples after catalytic reaction, which could explain the observed deactivation of re-used samples.

Table 6
Study of the reusability of HTc-Zn catalyst in the preparation of GC from urea and glycerol.

Entry	Cycles	Glycerol conversion (%)	GC yield (%)	GC selectivity (%)
1	1	82	72	88
2	2	80	65	81
3	3	81	64	80
4	4[a]	79	65	82
5	5[b]	76	60	79

All experiments were carried out using 5 wt% of catalyst with respect to glycerol, at 30 Torr and 145 °C, for 5 h.
[a] The catalyst was extracted with MeOH in a soxhlet.
[b] The catalyst was calcined at 450 °C during 6 h in an air flow, and then with a N$_2$ flow during 6 h.

Table 7
BE and surface composition determined by XPS on fresh and used samples.

Sample	BE (eV)							Surface composition
	C1s	O1s	Al2p	Zn2p	Sn3d	Mg2	Si2p	O:C:(Al:Zn:Sn:Mg:Si)
HTc-Zn[a]	291.4	536.6	79.6	1027.5	–	–		59.4:3:12.1:25.5:–:–:–
Fresh	295.8	533.2						
HTc-Zn[a]	291.4	536.4	79.06	1026.45	–	–		57.1:28.4:8.7:5.7:–:–:–
Used	294.7	533.4	77.76					
Sn-Beta[b]	285.2	533.3	–	–	488.2		104	64.0:1.36:–:–:0.37:–:34.2
Fresh	292.6	529.7						
Sn-Beta[b]	286.9	533.3	–	–	487.5		104	60.9:12.27:–:–:0.2:–:26.6
Used	290.3	530.7						
MgO[c]	290.1	534.3	–	–	–	92.8		50.4:3.8:–:–:–:45.7:–
Fresh	293.4				–			
MgO[c]	289.1	534.6	–	–	–	91.6		49.8:35.9:–:–:–:14.5:–
Used	292.7				–			

[a] Charge correction to C1s = 291.364 eV.
[b] Charge correction to Si2p = 1044 eV.
[c] No charge correction have been applied.

4. Conclusions

In order to avoid the formation of by-products, the transesterification reaction between EG and glycerol to give glycerol carbonate has to be carried out at temperatures as low as possible. Calcined hydrotalcites with $pK_a > 14$ [36] which are able to abstract a proton from glycerol are suitable materials to perform the transesterification giving high yields of GC. On the other hand, the regenerated hydrotalcite with Bronsted basicity gives lower selectivity owing to a higher production of glycidol.

Increasing the Lewis basicity of the mixed Mg–Al oxides derived from hydrotalcites by substituting the Mg by Li allows to work at much lower temperatures and catalyst loading than with the Mg–Al mixed oxide (35 instead of 50 °C), and (0.5 instead of 7 wt%). In addition the mixed oxide obtained by calcination of a mixture of $CaCO_3 + Al(OH)_3$ resulted the most effective catalyst for the transesterification reaction giving selectivities of 98% to GC.

Finally, the carbonylation of glycerol with urea is better carried out with solid catalysts with well balanced acid–base, in where Lewis acid activates the carbonyl of the urea and the conjugated basic sites activate the hydroxyl group of the glycerol. While ZnO has been reported as a catalyst with an adequate acid–base pair, it has been observed here that if the basicity of the conjugated base of ZnO is increased by preparing a Zn–Al mixed oxide with a higher conjugated base pair strength than ZnO, the reaction selectivity and final yield to GC significantly increase working with an urea to glycerol ratio of 1 mol mol^{-1}. This allows to substitute the soluble and difficult to recycle ZnO reported by the heterogeneous Zn–Al hydrotalcite catalyst reported here.

Acknowledgments

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