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In this work, we report a selective and straight process to synthesize glycerol carbonate from urea and glycerol using a simple and not commercially available catalyst (i.e. Sn(OH)₂). This catalyst was generated *in situ* from the reaction of Sn(II) halides and urea along the glycerol carbonatation process. Effects of main reaction parameters (i.e., temperature, molar ratio urea to glycerol, catalyst concentration) were investigated. Different tin halides were assessed as catalytic precursors, being the SnCl₂ the most efficient. We have found that Sn(OH)₂-catalyzed glycerol carbonatation reactions with urea achieved high conversions and selectivity (*ca.* 87 and 85 %, respectively). The samples of Sn(OH)₂ generated *in situ* or previously synthesized were equally active and selective catalysts toward glycerol carbonate have been successfully reutilized without loss activity. This is a very attractive route based on two inexpensive and readily available feedstock in a chemical cycle that overall, results in the chemical fixation of carbon dioxide and concomitantly, add value to the glycerol, a biodiesel byproduct.

Introduction

In recent years, the biodiesel industry has generated glycerol in large surplus, a fact that has motivated the search by processes that can aggregate value to this inexpensive, abundant and renewable feedstock.¹ The utilization of glycerol as a biorefinery platform molecule constitute an opportunity to obtain higher value-added products from an available and inexpensive raw material. Among the several glycerol derivative products, the glycerol carbonate has gained prominence in the last two decades due to its wide use spectrum.²

Glycerol carbonate is a green solvent with high a boiling point, low toxicity, great biodegradability, being used as the solvent in the field of medicine, paints, cosmetics, electrolyte in the lithium batteries, in addition to be an ingredient in the surfactant synthesis, polymers, drugs, and agrochemicals.²⁻³ Therefore, the synthesis of glycerol carbonate representing a promising pathway for the valorization of bio glycerol generated as biodiesel waste.⁴

The main difference between the routes to produce glycerol carbonate consists in the choice of which will be the reactant used to incorporate the carbonyl group to the glycerol.⁵⁻⁷ On this sense, the alkaline transesterification of glycerol with

⁺ Footnotes relating to the title and/or authors should appear here. Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x dimethyl or diethyl carbonate has been a route very employed to produce glycerol carbonate.⁸⁻¹⁰ Several alkaline catalysts (i.e., based on the mixture of Mg and Ca oxides) have been successfully used, giving 100 % glycerol carbonate after 1. 5 h reaction at 343 K.¹¹ Nevertheless, the alkyl carbonates utilized in the transesterification are typically generated via phosgene reactions, an environmentally unfriendly reactant.¹²

The carbonylation of glycerol using CO or CO_2 is very promising from the environmental viewpoint.¹³ Copper salts have been extensively used in oxidative carbonylation of glycerol.¹⁴⁻¹⁶. However, there are limitations, such as the high toxicity of CO, the high pressures required. In addition, poor yields have been obtained in the reactions with CO_2 due to the thermodynamic limitations, which compromise these processes.¹⁷

Alternatively, the use of urea as a carbonylic source to produce glycerol carbonate have shown an attractive phosgene-free route.¹⁸ Urea is an inexpensive and commercially available reactant. The reactions of carbonatation of glycerol with urea have been efficiently catalyzed by Lewis acid such as salts and oxides of transition metals.¹⁹⁻²² In addition to use a high load of catalyst metal, some of these processes undergo with a low intrinsic activity and poor selectivity.

Solid-supported Keggin heteropolyacids (i.e. $H_4SiW_{12}O_{40}/MCM$ -41 or $H_4SiW_{12}O_{40}/H\beta$ -zeolite) are efficient catalysts on the carbonatation of glycerol with urea.^{23,24} Similarly, solid-supported transition metal catalysts have been also successfully utilized in urea glycerolize reactions.²⁵

Tin based catalysts are also utilized in synthesis of glycerol carbonate. Srikanth et al. synthesized Cs-exchanged Keggin heteropolyacid catalysts impregnated with Sn(II) different loads (i.e., Sn-Cs₃PW₁₂O₄₀), and evaluated their activity in the synthesis of glycerol carbonate from urea.²⁶ Those authors

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found that at 413 K temperature and under vacuum, the reactions achieved high conversion and selectivity toward glycerol carbonate (*ca.* 91 and 81 %, respectively). Lingaiah et al. assessed the urea glycerolize over tin-tungsten mixed oxide catalysts prepared by precipitation method and verified that using a 2:1 molar ratio of Sn to W, ca. 52 % of glycerol was converted with a high carbonate selectivity (ca. 95 %).²⁷

Although all the catalysts described by us herein until now were synthesized in the laboratory, available commercially Lewis acid catalysts are also an attractive option in reactions of urea alcoholysis. In special, tin(II) halides demonstrated to be efficient catalysts in reactions of urea with terpenic alcohols.^{28,29} These tin(II) halides are easily handling solids, have high water tolerance and low cost, have been successfully used in several reactions to valorize glycerol.^{23, 30-32}

Inspired by these findings, in this work we investigate the catalytic activity of tin(II) halides in reactions of urea glycerolize to synthesize glycerol carbonate. Although our initial intention has been to assess the activity of tin(II) halides in carbonatation of glycerol with urea, we have found that at reaction conditions studied, those compounds were converted to Sn(OH)₂. Therefore, we demonstrate that Sn(OH)₂-catalyzed reactions were a selective and straight synthesis pathway to obtain glycerol carbonate from urea and glycerol. The effects of main reaction parameters (i.e. temperature, molar ratio of urea to glycerol, nature of pre-catalyst, catalyst concentration) were investigate in solvent-free processes carried out under air flux.

Experimental

Chemicals

All chemicals and solvents purchased from commercial sources and used as received. All tin (II) salts (SnCl₂ (ca. 98 wt. %), SnF₂ and SnBr₂ (ca. 99 wt. %)) were acquired from Sigma-Aldrich, as well the glycerol (ca. 99.5 wt. %). Urea was GE (99.5 wt. %). Methyl alcohol was Vetec (ca. \geq 98.9 wt. %).

Sn(OH)₂-catalyzed urea hydrolysis reactions with glycerol

The catalytic runs were performed in a 25 mL three-necked glass flask, equipped with sampling system, a reflux condenser, in thermostatic bath with magnetic stirrer. Typically, urea (34.3 mmol) was added to pure glycerol (34.3 mmol), which were stirred and heated to 413 K; then, after the adding Sn(II) pre-catalyst (ca. 4.9 mol %), the reaction was started. The air flow used was 415 cm³min⁻¹.

Reaction monitoring

The reaction progress was followed taking aliquots at regular intervals and analyzing them via gas chromatography (Shimadzu GC-2010 Plus, FID), fitted with RTX-Wax capillary column (0.25 μ m x 0.25 mm x 30 m)). The temperature program was as follows: 150° C/ 3 min, 10° C/min up to 230° C, then 5° C/min up to 250° C hold time of 3 min. Both injector and detector were kept at 250°C temperature, respectively. Hydrogen was the carrier gas (ca. 1.2 mL min⁻¹). The conversion and reaction yields were calculated by matching the GC peak areas of the pure compounds (i.e., glycerol and glycerol carbonate, respectively) in the calibration curves. Because it

is a solvent free reaction, the samples were diluted in methylalcohol before GC analyses. DOI: 10.1039/C8NJ05635H

Purification and product identification

Glycerol carbonate was purified trough liquid-liquid extraction procedures (Fig SM1). The mass spectrum of the GC was obtained on a Shimadzu MS-QP 2010 Ultra mass spectrometer instrument, coupled to Shimadzu 2010 GC (Tokyo, Japan) with He as the carrier gas (ca. 1.18 mL min⁻¹). Column and chromatographic conditions were the same of the GC analyses. The injector and MS ion source temperatures were 250 and 200 °C, respectively. The MS detector operated in the EI mode at 70 eV, with a scanning range of m/z 0-400. The ¹H and ¹³C NMR spectra was recorded on the Mercury-300 Varian Spectrometer at 300 and 75 MHz respectively, in CDCl₃ solution. FT-IR/ ATR spectroscopy analysis was recorded in Varian 660 FT-IR Spectrometer. The spectroscopic data of the glycerol carbonate are shown as follow (Fig 1).



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Fig. 1 4-(hydroxymethyl)-1,3-dioxolan-2-one (glycerol carbonate)

FT-IR/ ATR (v (cm⁻¹)/ attribution): 3365/ (v OH); 2881-2935/ (v CH₂ and CH); 1774/ (v C=O cyclic 5-membered carbonate); 1170/ v C-C); 1043/ (v C-O of C-OH bond).

GC-MS ((m/z)/relative intensity): 88/ 22, 87/ 31, 44/ 95, 43/ 100, 31/ 77 and 29/ 34.

¹H NMR (300 MHz, CDCl₃) δ (ppm): 3.60-3.78 (m, 1H, H-6'*), 3.89-4.08 (m, 1H, H-6*), 4.24-4.63 (m, 2H, H-5), 4.65-4.96 (m, 1H, H-4), 5.43-5-48 (m, OH). *signals may be exchanged.

¹³C NMR (75 MHz, CDCl₃): δ (ppm); 61.8 (C-5); 65.9 (C-6); 76.7 (C-4); 155.5 (C-2).

Characterization of $Sn(OH)_2$ generated in situ in the reactions of urea glycerolize

The tin content on the solid recovered from the reaction was confirmed by AAS using an Agilent Atomic Absorption Spectrometer, model Spectra 240FS AA. Samples were digested with HCl at room temperature. Thermal gravimetric analysis (TGA) of the solid generated during the reaction was conducted by a Simultaneous Thermal Analyzer (STA) 6000 Perkin Elmer (Fig.SM2). To do it, the solid sample (ca. 3.990 mg) was heated from 30.0 to 850.0 °C at a rate of 10.0 °C min⁻¹, under N₂ flux (50.0 mL min⁻¹). FT-IR/ATR spectroscopy analyses were carried out in Varian 660 FT-IR Spectrometer (Fig. 2). To verify the possible presence of organic compounds in the solid formed during the reactions, elemental analysis was done using a Perkin-Elmer CHN analyzer.

The structural properties were measured on the Quantachrome NOVA 1200 apparatus, using the vacuum degasser at 80 $^{\circ}$ C for 5 h. The BET surface area was determined from MultiPoint BET. The size and pore volume distribution were obtained from the BJH model (Table SM1).

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Results and discussion

General aspects

The carbonatation of glycerol with urea is a reversible reaction (Scheme 1), which generally requires temperatures higher than 413 K.²¹ Although at these temperatures, it occurs without a catalyst, its presence is a key aspect for that a high yield of glycerol carbonate can be obtained.



Scheme 1. Glycerol carbonate formation via urea glycerolize

Table 1. Metal-catalyzed urea glycerolize reactions

Catalysts	Con.	Sel.	Time	Т	Removal	Pof
(mol %)	(%)	(%)	(h)	(K)	NH₃	Rel.
^a Au/ support/ (0.02 Au ³⁺)	81	68	4	423		
^a ZnSO ₄ / (1.0 Zn ²⁺)	83	58	4	423	N ₂ flux or vacuum	17
^a MgO/ (4.14 Mg ²⁺)	59	37	4	423		
^b (RIm) ₂ ZnX ₂ / (1.0 Zn ²⁺)	93	93	6	413	vacuum (14.7 KPa)	30
^b Na ₄ SiW ₁₂ O ₄ ₀ /MCM-41 (0.1 SiW ₁₂ O ₄₀ ⁴⁻)	75	77	8	423	N ₂ purge	31
^b Zn ²⁺ salts/ (2.0 Zn ²⁺)	85	93	2	423	2.67 kPa	21
^b La ₂ O ₃ / (0.37 La ³⁺)	69	98	1	413	3 kPa	32
⁰PS- (Im)₂ZnX₂/ (0 3 Zn²+)	93	93	6	413	14.7 kPa	23
^b SnO ₂ /WO ₃ / (6.0 Sn ⁴⁺)	52	95	4	413	Reduced pression	27
^b Zn ²⁺ salts (3.7)	84	97	3	413	3 kPa	33
Sn(OH)₂/ (4.9 Sn ²⁺)	87	85	4	413	Air flux	This work



Several solid supported metal catalysts or soluble have been used in reactions of glycerol carbonatation with urea. Table 1 summarizes some important examples. Different approaches have been used to remove ammonia from reaction medium (Table 1). Zinc, molybdenum, tungsten and tin are the most used catalysts in reactions to synthesize glycerol carbonate (Table 1). In general, the reactions are carried out at temperatures of 413 or 423 K, under reduced pressure or vacuum, being the ammonia removed throughout the process (Table 1).

Catalytic tests: a quick in situ conversion of homogeneous catalyst SnCl₂ to solid catalyst Sn(OH)₂ DOI: 10.1039/C8NJ05635H

Tin(II) halides have been efficiently used as catalysts in several reactions to add value to the glycerol such as esterification and ketalization.³⁴⁻³⁶ However, as far we know, they were not assessed in glycerol carbonatation reactions with urea. Herein, initially we carried out the reactions in the presence SnCl₂ as catalyst (Fig. 2).



Fig. 2 Kinetic curves of urea glycerolizes in the presence and absence of $SnCl_2$ (a) and conversion/ glycerol carbonate selectivity (b)^a

^aReaction conditions: glycerol (34.3 mmol); urea (34.3 mmol); temperature (413 K); Sn(II) concentration (4.9 mol %); air flow (415 cm³min⁻¹).

We have found that the after 2 min, the addition of the SnCl₂ triggered the formation of a white solid. The solid formed was removed from the reaction, washed with hot water, dried at 373 K, and identified by elemental analysis (i.e., AAS), and FT-IR spectroscopy analyses as Sn(OH)₂ (Scheme 2). AAS analysis of liquid phase collected from reaction indicated the absence of tin(II), which reinforce the total presence of the tin in the formed solid.



Scheme 2. Formation of $Sn(OH)_2$ from reaction of $SnCl_2$ with urea at 413 K in net glycerol

Figure 3 shows a comparison of FT-IR/ATR spectra obtained from two samples of Sn(OH)₂; the first one formed **on the urea glycerolize** reaction and second sample that was previously synthesized.

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explain the formation of Sn(OH)₂. The release of an monia from urea can raise the pH of the reaction Medlum, 34300Mg6fflehydrolysis of Sn(II) as shown in Scheme 3.³² Therefore, tin(II) hydroxide could be formed as describes the Equation 1.

 $SnCl_{2(s)} + 2NH_{3(aq)} + 2H_2O_{(I)} \rightleftharpoons Sn(OH)_{2(s)} + 2 NH_4^+_{(aq)} + 2Cl^-_{(aq)}$

Equation 1

Equation 1 explains why the formation of $Sn(OH)_2$ only was observed in the presence of both glycerol and urea, an experimental data verified by us. These two reactants provide water and ammonia that allow $SnCl_2$ hydrolysis to $Sn(OH)_2$. Therefore, some additional experiments were performed aiming to compare the activity of solid formed (i.e., $Sn(OH)_2$), with the activity of previously synthesized $Sn(OH)_2$. These reactions were performed and compared with that where initially $SnCl_2$ was added to the reactor (Table 2). Our intention was to confirm if the $Sn(OH)_2$ that was formed in situ will be as active as the $Sn(OH)_2$ synthesized in the laboratory.

 Table 2. Conversion and selectivity of Sn(II)-catalyzed urea

 glycerolize reactions^a

Run	Catalyst	Glycerol conversion (%)	Glycerol carbonate Selectivity (%)
1	SnCl ₂	83	73
2	Sn(OH)₂ (generated <i>in situ</i>)	81	71
3	Sn(OH)₂ (previously synthesized)	83	73

^aReaction conditions: glycerol (34.3 mmol); urea (34.3 mmol); temperature (413 K); Sn(II) (4.9 mol %); time (4 h); air flow (415 $cm^3 min^{-1}$).

Table 2 reinforced the hypothesis that the $Sn(OH)_2$ efficiently catalyzes the urea glycerolize. No significant difference was observed in reactions with $Sn(OH)_2$ generated in situ or previously synthesized. In addition, the conversions and glycerol carbonate selectivity achieved on these reactions (entries 2,3, Table 2) were likewise that obtained in the reaction started with the $SnCl_2$ as a catalyst (entry 1, Table 2).

Mechanistic insights

Previously, we have detected the presence of isocyanic acid (HN=C=O) as an intermediate in carbonylation reactions involving urea.^{28,29} However, in this present study it was not detected. Aresta et al. had a similar result when investigate the urea glycerolize in the presence of insoluble metal catalysts (i.e., titanosilicates and zirconium phosphates).³⁸ Those authors proposed that the urea may react directly with the glycerol, leading the ammonia detachment and formation of glycerol carbonate. Because it is an insoluble catalyst, the urea activation may be occurring through surface phenomena (*i.e.*, adsorption). Therefore, herein we suppose that the activation of urea by the Sn(OH)₂ catalyst and the consequent glycerol

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Fig. 3 Comparison of FT-IR/ATR spectra of the $Sn(OH)_2$ that was recovered from urea glycerolizes reaction and the previously synthesized $Sn(OH)_2$

The absorption bands at 469 cm⁻¹ and 528 cm⁻¹ are characteristics of Sn-O bond stretching, while the absorption bands at wavenumber 3307 $\rm cm^{-1}$ and 1040/731 $\rm cm^{-1}$ are assigned to the O-H bond stretch and bend respectively (Fig 3).³⁸ The Sn content of 77.15% found by AAS in the solid after treatment reasonably agrees with the expected theoretical Sn content for Sn(OH)₂, which is 77.73%. Powder XRD analysis revealed that the Sn(OH)₂ catalyst is amorphous. This result agrees with literature³⁹. The analysis thermal of Sn(OH)₂ was carried out (Fig. SM2). We have found that two events of mass loss were observed at two temperature ranges distinct; 30 to 240 °C and 250 500 °C. Literature assigned the first one to the loss of water and the second one to the decomposition of hydroxide to tin oxides [39]. The textural properties were analyzed (Table SM1). We have found that surface area of in situ generate Sn(OH)₂ catalyst and previously synthesized were 18.4 and 16.0 m²g⁻¹ (Table 1SM). Although these values are low if compared to the solids, it is higher than the surface area of precursor halides. Probably, it was a positive aspect that favored the activity of catalyst. Elemental analysis of CHN were important to assure that no organic or nitrogen ligand was coordinated to the in situ generate tin catalyst.

The results obtained by AAS and FT-IR/ ATR and in the catalytic tests for the solid that was *in situ* generated allow us to propose that after addition of SnCl₂ to the reaction medium, it is rapidly converted to Sn(OH)₂. The formation of Sn(OH)₂ may be explained by SnCl₂ hydrolysis by water present in the reaction medium. The precipitation of Sn(OH)₂ was verified even under dry N₂ flow, which implies that this *in situ* formation is not related to H₂O from the air flow.

At the reaction beginning of the urea with glycerol, the only water present in the medium is the hydration water of SnCl₂ catalyst; however, during the carbonatation process, it is possible that parallel reactions such as oligo-polymerization of glycerol may be occurring, mainly due to high elevated temperature (*ca.* 413 K) and the presence of Sn(II) cations.³⁸ It is possible that the glycerol dehydration reactions produce enough water to complete the hydrolysis of SnCl₂ to Sn(OH)₂. The presence of the urea in the reaction is a key aspect to

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carbonylation may proceed through mechanism depicted in Scheme 3.

Initially, the urea may be activated by the coordination to the active site of catalyst (i.e., Sn(II)). The urea activation makes the carbonylic carbon of urea more electrophilic, facilitating its nucleophilic attack by the glycerol hydroxyl group (I), leading to the formation of carbamate intermediate (II), and releasing an ammonia molecule. These carbamate intermediates were 10 detected by GC-MS analysis (Fig. SM3). 11

In the next step, since that the carbamoyl group of intermediate (II) is still activated, there is another ammonia molecule releasing giving the cyclic carbamate intermediate (III). This intermediate reacts with urea providing the glycerol carbonate (IV), which is liberated, allowing the coordination of another molecule of urea and the continuity of cycle.



Scheme 3. Sn(OH)₂-catalyzed urea glycerolize reaction (adapted from ref. 40).

The in situ formation of Sn(OH)₂ from Sn(II) commercial salts represents a major advantage of this process since this compound is not commercially available. In addition, it can be recovered and reused in the reaction.

Effects of Sn(II)-pre-catalyst nature on Sn(OH)₂-catalyzed urea glycerolize reaction

We evaluated the Sn(OH)₂ activity in urea glycerolize reactions, in which it was generated from different commercial tin(II) halides (i.e. SnF₂, SnCl₂ and SnBr₂). The kinetic curves and the main selectivity results and conversion are presented in Fig 4 and Table 3, respectively.



Fig. 4 Kinetic curves of Sn(II)-catalyzed urea glycerolize with different tin(II) salts as the pre-catalysts^a

^aReaction conditions: glycerol (34.3 mmol); urea (34.3 mmol); temperature (413 K); Sn(II) (4.0 mol %); air flow (415 cm³ min⁻¹)

The different salts of Sn(II) tested on reactions showed a similar behavior in terms of glycerol conversion, which were almost equal statistically. All the commercial salts that were tested as pre-catalysts allowed to achieve selectivity greater than 71 % for the glycerol carbonate (Table 3).

In the absence of catalyst, the oligomers were the main products (entry 1, Table 3). During the reaction, the solution became light brown. This observation suggests that products likewise glycerol oligomers, or products formed from glycerol carbonate oligomerization (i.e., 2-oxo-1,3-dioxolan-4-yl) methyl carbamate, Scheme 4, detected by GC-MS analysis), may be also occurring along the reaction (Fig SM4).

Table 3 Effect of the nature of tin(II) pre-catalyst on Sn(OH)2catalyzed urea glycerolize^a

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Ru n	Pre- cataly st	рН	Conv. (%)	Selectivity (%)		Pric e ^c (US\$ /100 g)
		data		Glycerol carbonat e	oligom. ^b	-
1	-	6.0	40	28	72	-
2	SnCl ₂	0.6	83	73	27	57
3	SnF_2	2.7	77	74	26	89
4	SnBr ₂	0.2	70	71	29	767

^aReaction conditions: glycerol (34.3 mmol); urea (34.3 mmol); temperature (413 K); Sn(II) concentration (4.0 mol %); air flow (415 cm³min⁻¹)

^bOligomers of glycerol, not detected by GC but calculated by mass balance

^cPrice of Sigma-Aldrich

It is known that decrease on pH value is consequence of hydrolysis of anion present in the tin(II) halide, which release HX. Indeed, the pH measurements agree with the strength of Bronsted acid released, which increase with increase of anion radium. However, no correlation of pH value and conversions data was noticed. Probably, the ammonium generated along

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the reaction neutralize the acids, consequently the reaction was not affected by the initial pH value. Indeed, tin halide is converted to $Sn(OH)_2$, which is the true catalyst.

Indeed, in the production of glycerol carbonate, oligomeric products are always formed as secondary products.⁴² Oligomers have low volatility and are undetectable by GC analyses. Herein it was calculated from reaction mass balance (Scheme 4).⁴²



Scheme 4. Formation of (2-oxo-1,3-dioxolan-4-yl) methyl carbamate (c) from GC (a) and urea (b)

Conversely, when the Sn(II) pre-catalysts (*ca.* 4.9 mol % Sn²⁺) are added to the reaction medium, the catalyst Sn(OH)₂ is quickly generated promoting a significance enhancement on conversion and reaction selectivity, practically doubles the glycerol conversion. This makes the Sn(OH)₂ a promising catalyst to synthesize the glycerol carbonate from urea.

All commercial salts tested as pre-catalysts allowed to achieve selectivity greater than 71 % for the glycerol carbonate under the conditions evaluated (Table 3). When we compare the results of conversion and glycerol carbonate selectivity presented in Table 1 to that obtained in Sn(OH)₂-catalyzed reactions, we can conclude satisfactory results were achieved by a system that presents a simple and reusable catalyst, which avoid the use of vacuum, reduced pressure or inert atmosphere.

Effect of catalyst concentration in $Sn(OH)_2$ -catalyzed urea glycerolize reaction

The SnCl₂ was the pre-catalyst investigated, with a load varying from 1.2 to 6.1 mol %. (Fig. 5). In general, an increase of catalyst load resulted in a higher initial rate as well as a greater final conversion until 4.9 mol % (Fig 5).



Fig. 5 Effect of Sn(II) catalyst load on urea glycerolize^a ^aReaction conditions: glycerol (34.3 mmol); urea (34.3 mmol); pre-catalyst (SnCl₂), (413 K); air flow (415 cm³ min⁻¹).

When a catalyst load was higher than 4.9 mol % (i.e. g_{rrc} , i.m.) %), a reduction on reaction conversion % is 10 ks 4 (Fig 35)! This effect was also verified in a previous work where SnCl₂ was the catalyst on urea alcoholysis with β -citronellol.²⁹ Probably, the formation of agglomerated particles resulting of the large amount of the insoluble solid makes difficult the access of the reactants to the catalyst active sites and prevent a better diffusion of the reagents in the reaction medium.

The glycerol carbonate selectivity remained practically constant when increasing the amount of catalyst except for the 6.1 mol % (Fig. 6). This means that in the presence of $Sn(OH)_2$ improves the glycerol conversion without significantly affect the reaction selectivity only until 4.9 mol % of catalyst.



Fig. 6. Effect of $Sn(OH)_2$ catalyst concentration on reactions of glycerol carbonatation with urea^a

^aReaction conditions: glycerol (34.3 mmol); urea (34.3 mmol); temperature (413 K); air flow (415 cm³ min⁻¹). SnCl₂ as precatalyst (4.9 mol %)

Effect of temperature on the Sn(OH)₂-catalyzed urea glycerolize

Since the catalytic process studied here occur in a liquid phase reaction under high temperatures (Table 1), we consider the possibility of reagents and or products could be also migrating to the vapor phase. Then the liquid-vapor equilibrium (LVE) prediction of the mixture glycerol and urea at 1 atm was performed (Fig. 4 SM). The simulations were done using Aspen Plus 8.8 software and showed that temperatures higher than 487 K are greater than the bubble point of the blend 1:1 urea glycerol. It is a temperature very higher than those used herein. The phases composition of the different temperatures tested, under equilibrium conditions and considering a glycerol conversion of 85 %, were predicted by simulations using the IDEAL method as an estimation of component properties, also in Aspen Plus 8.8 (Fig. 7).

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Fig. 7 Prediction of composition of the vapor and liquid phases (i.e., glycerol and glycerol carbonate) at various temperatures

The boiling point of glycerol carbonate is 410 K when pure. The simulation results (Fig. 7) predict that the reactants glycerol and urea vapor phase increase with increasing temperature. About 40 % of the glycerol carbonate would be in the vapor phase at 413 K, and that at 423 K great part would be in the vapor phase (*i.e.*, 59 %). Although we have used a reflux condenser coupled to the reactor, we done some experiments to verify if any loss of glycerol carbonate occurred during the reactions.

Results obtained from gas phase condensation removed by the air flux showed that a maximum of 3 % of glycerol carbonate can be loser during the process, which has a minimum effect over the values obtained and presented by us.

The effect of temperature on the conversion and selectivity of carbonatation of glycerol with urea was evaluated and the kinetic curves are shown in Fig 8. In general, the glycerol was more remarkably converted when the temperature was increased in the range of 393 to 413 K. However, the reactions carried out at 423 and mainly 433 K reached lower conversions (Fig. 8a).

In terms of glycerol carbonate selectivity, this decreasing was more remarkable (Fig. 8b). This behavior suggests that at these reaction conditions (*ca.* 423 K), the glycerol carbonate begins to be consumed in parallel reactions, such as polyurethanes or polyisocyanates (Scheme 4).^{40,41}



Fig. 8 Effect of temperature on conversion (a) and glycerol carbonate selectivity (b) of Sn(OH)₂-catalyzed urea **glycerolize**^a ^aReaction conditions: glycerol (34.3 mmol); urea (34.3 mmol); SnCl₂ as pre-catalyst (4.9 mol %); air flow (415 cm³ min⁻¹).

The results further reinforce that the $SnCl_2$ addition to urea glycerolizes reaction *in situ* generating $Sn(OH)_2$ is a key aspect of achieving high glycerol conversion values (Fig. 8) and that the temperature of 413 K is the smallest and most suitable for glycerol conversion to carbonate glycerol.

Effect of reactants molar ratio urea to glycerol on the Sn(OH)₂catalyzed urea glycerolize

The reactants molar proportion effect on the conversion and selectivity was evaluated in the proportion of 1: 1, 1: 1.5 and 1: 2 of glycerol: urea. We note that as well as the initial conversion rate (*i.e.* not shown here), the conversion after 4 h of reaction was not affected by the variation in the ratio between the reactants, in the presence of catalyst.

On the other hand, an increases of the urea amount in the reaction increased the conversion of the glycerol in the absence of catalyst (Fig. 9).

The selectivity of glycerol carbonate decreased when the amount of urea was increased. This was already expected due to the formation of polymers from urea and glycerol at elevated temperatures, as discussed before. This result justifies the use of 1: 1 molar proportion, because it has maintained the carbonate selectivity as high as possible. Among the molar proportions evaluated, 1: 1 glycerol: urea also represents a greater economy, in view of the lower consumption of urea.

SnCl₂-catalyzed urea glycerolizes: The need of air flow in the reaction of urea glycerolize

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In order to reach higher conversion values for glycerol and GC selectivity, we must displace the equilibrium of the reaction by withdrawing the formed ammonia. For this, it is usual to work with reduced pressures or nitrogen flow (Table 1), however we opted for a simpler alternative and we have used air flow.



Fig. 9 Effect of molar proportion glycerol to urea on Sn(OH)₂catalyzed urea glycerolize^a

^aReaction conditions: glycerol (34.3 mmol); time (4 h); SnCl₂ as pre-catalyst (4.9 mol %); T (413 K); air flow (415 cm³ min⁻¹).

In general, we noticed that the removal of ammonia from the reactor with an air flow during the process shifts the reaction equilibrium toward formation of glycerol carbonate (Fig. 10). In the absence of air flow, only a low glycerol carbonate selectivity was achieved, favoring the formation of oligo-polymers (Table 4). From the air flow of 880 cm³min⁻¹, the selectivity of glycerol carbonate begins to decrease, which is due to the drag of this product outside the reactor along with the ammonia, due to the high rate of the air flow.



Fig. 10 Effect of air flow on Sn(OH)₂-catalyzed urea **glycerolize**^a ^aReaction conditions: glycerol (34.3 mmol); urea (34.3 mmol); SnCl₂ as pre-catalyst (4.9 mol %); temperature (413 K).

The air flow also increased the glycerol conversion (Fig. 10), however, it has been observed that this occurs only up to a

certain flow (*ca*. 880 cm³ min⁻¹), from which the conversion stops to rise. DOI: 10.1039/C8NJ05635H

The increase of conversion and selectivity could be also related to lower ammonia competition for the Lewis acid sites of the catalyst. Because ammonia is a Lewis base, it could definitively bind to the Sn(II), a Lewis acid, causing a reduction of its catalytic activity. This undesirable effect is already known in the Pd(II)-catalyzed urea alcoholysis reaction.⁴² Those authors circumvented this problem adding Ag(I) cations to the solution. Herein, in the Sn(OH)₂-catalyzed urea glycerolizes under air flow, it was unnecessary. With an airflow of 880 cm³min⁻¹, it was possible to obtain a glycerol conversion of 87 % and at the same time a glycerol, carbonate selectivity of 85 %.

 Table 4. Effect of air flow effect on Sn(OH)₂-catalyzed urea

 glycerolize reaction^a

Evn	Air flux (cm ³ min ⁻¹)	Conversion (%)	Selectivity (%)		
Exp.		Conversion (%)	GC	Oligomers	
1 ^b	0	27	16	82	
2	415	83	73	27	
3	880	87	85	15	
4	1680	90	76	24	

^aReactions conditions: glycerol (34.25 mmol); time (4 h); SnCl₂ as pre-catalyst (4.9 mol %); temperature (413 K) ^bNo catalyst

Comparing the results obtained by variation of the air flow (Table 4) with the results presented in the literature (Table 1), it was verified that the conversion values reached are close to the higher conversions already described. It is noted that zinc compounds such as Zn(II) salts (*i.e.*, ZnCl₂) provided high selectivity and conversion of glycerol to glycerol carbonate, higher than those obtained with Sn(II) catalyst.⁴³ However, such processes used higher temperatures, vacuum or N₂ (more expensive that the air flow) or occurred in homogeneous phase, hindering the catalyst recovery. The use of air flow combined with insoluble **in situ** generated Sn(OH)₂ considerably reduces the cost of the process.

Conclusions

A simple, economical and solvent-free process for the synthesis of glycerol carbonate via urea glycerolize was achieved, using SnCl₂ as a pre-catalyst to generate in situ the solid Sn(OH)₂ catalyst. In the presence of the Sn(OH)₂ solid catalyst (4.9 mol % Sn), and an air flow (880 cm³ min⁻¹) for the removal of ammonia, a high glycerol conversion (ca. 87%) and GC selectivity (ca. 85 %) was obtained after 4 h of reaction at 413 K. In the absence of catalyst, the polymerization reactions of glycerol and carbonate were favored. The pre-catalyst SnCl₂ is a commercially available and inexpensive reactant. Tin(II) catalyst efficiently allow the use of urea as an indirect CO₂ source. Solid Sn(OH)₂ that was generate in situ from SnCl₂ and urea is not commercially available. This is an insoluble compound in the reaction medium, which was easily recovered by filtration and reused as catalyst. AAS analysis has shown that after solid catalyst formation there is no leaching of Sn, which makes the catalysis completely heterogeneous.

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Conflicts of interest

There are no conflicts to declare.

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