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Synthesis of di-*n*-butyl carbonate from *n*-butanol: Comparison of the direct carboxylation with butanolysis of urea by using recyclable heterogeneous catalysts

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ABSTRACT

The synthesis of di-*n*-butyl carbonate has been studied starting from *n*-butanol and either CO_2 or urea. A comparison of the two synthetic routes is reported. Several mixed oxides have been synthesized and tested with the aim of finding a catalyst active in mild conditions (T, t), recoverable and reusable. Different strategies to push the reaction toward the formation of the target product (di-*n*-butylcarbonate) have been applied and adapted to each case. The pervaporation membrane and chemical water traps are compared as techniques for water elimination and equilibrium shift in the direct carboxylation. Among the tested catalysts, $0.03Nb_2O_5/CeO_2$ is the best in the case of the direct carboxylation of butanol, whereas 0.5MgO/ZnO results the best in terms of activity and robustness for the alcoholysis of urea.

1. Introduction

Dialkyl carbonates are chemicals largely used in the chemical and polymer industry. Finding new synthetic methodologies, which respond to the requisites of sustainability, is of paramount importance for the chemical industry. In this paper, we focus on di-*n*-butylcarbonate (D^nBC), a member of the dialkylcarbonates family, that finds application as solvent and is an important chemical intermediate for the synthesis of organic compounds [1]. D^nBC is also used as phosgene substitute for polycarbonates synthesis [2], as base material for lubricants, for metal degreasing and leather processing [3].

D^nBC is generally prepared *via* synthetic routes such as: phosgenation [1,4], oxidative carbonylation of butanol [5–7], transesterification of other carbonates [8–18]. Although phosgene technology is quite safe today, $COCl_2$ is banned in several countries and, most important, cannot be transported. The carbonylation process has drawbacks due to the use of chlorides and NO. In the transesterification process expensive precursors such as other dialkyl carbonates are required. However, new synthetic routes are wished which may be safer and more sustainable.

Dialkyl carbonates can be prepared from CO_2 through either the direct carboxylation of alcohols (Eq. (1)) [1,19–22] or the alcoholysis of urea, an active form of CO_2. (Eqs. (2a) and (2b)) ($\Delta G_f{}^{\circ}{}_{urea} = -197.5$ kJ/mol; $\Delta G_f{}^{\circ}{}_{CO2} = -394.4$ kJ/mol) Today urea represents over 65% of products industrially produced from CO_2 [23].

$$CO_2 + 2ROH \rightarrow (RO)_2CO + H_2O \qquad (1)$$

$$H_2NCONH_2 + ROH \rightarrow H_2NC(O)OR + NH_3 \qquad (2a)$$

$$H_2NC(O)OR + ROH \rightarrow (RO)_2CO + NH_3 \qquad (2b)$$

Although both the direct and indirect route based on CO_2 have an environmental impact much lower than the commonly used phosgenation and offer great advantage in terms of atom economy [24], they do not have industrial application because of some bottlenecks.

The direct carboxylation of alcohols (Eq. (1)) has thermodynamic limitations that cause low conversion yield. At $T > 400$ K the equilibrium concentration of the carbonate is as low as 0.1–1%, due to the fact that, although the ΔH is slightly negative, the adverse entropic factor due to the use of gaseous CO_2, which is found at the end in a liquid product, makes the ΔG positive [25].

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The removal of water in reaction 1 helps to shift the chemical equilibrium toward the carbonate, leading to better carbonate yields. Several organic and inorganic water traps have been used [26–28]. Attempts to remove water from the reaction mixture using pervaporation membanes in the case of ethanol have afforded interesting results [20d].

Alternatively, the alcoholysis of urea is a promising synthetic route [29–34] since urea is abundant (it is produced at over 180 Mt/y from CO_2), inexpensive, nontoxic, and environmentally friendly. Upon interaction of urea with alcohol [Eq. (2a)] a urethane is first formed, which is then transformed into the dialkyl carbonate. [Eq. (2b)] Reaction 2a easily occurs even in absence of catalysts and at lower temperatures than reaction 2b, which, instead, requires a catalyst. Metal oxides (such as ZnO, CeO_2, MgO, CdO, La_2O_3 [35]) are generally employed as catalyst under hard operative conditions (497–523 K, 7–20 h), which may affect the selectivity toward the carbonate and make complex the separation process.

Herein, we report a comparative study on the synthesis of D^nBC through the direct carboxylation of butanol and butanolysis of urea. In the latter case, considered the higher yield of conversion, we have also carried out a screening of different mixed oxides paying attention to their recoverability and recyclability.

2. Material and methods

Chemicals were purchased from Aldrich (RP). All the commercial metal oxides were calcined at 823 K for 3 h before use. Commercial urea was reduced to a fine powder and dried under vacuum before use in the reaction [36].

Pure D^nBC used for the calibration curve was obtained by transesterification of DMC with 1-butanol (*vide infra*).

Mixed oxides were prepared by High Energy Milling (HEM) at 700 rpm by using a Planetary Micro Mill Fritsch Pulverisette 7 equipped with an agata basket and balls. Alternatively the coprecipitation method was used, as specified.

GC–MS analyses were carried out with a gas chromatograph Shimadzu 17 A (capillary column: 30 m; MDN-5S; l 0.25 mm, 0.25 mm film) coupled to a Shimadzu QP5050A mass spectrometer.

Kinetic studies on the reactions were carried out using a gas chromatograph HP 6850 series equipped with a FID detector and a capillary column ZB-WAX (30 m, 0.25 mm).

Water content was measured by the Karl Fisher method, using a Metrohm 785 DMP Titrino apparatus.

Infrared spectra were obtained with a spectrometer SHIMADZU IR Prestige 21 using KBr discs. The sample was dispersed in Nujol.

Energy Dispersive X-ray diffraction (EDX) patterns were recorded at room temperature on a Shimadzu EDX-720/800HS, using a 5–50 kV Rh target X-ray generator and a Si (Li) detecting system. For noise reduction, the detector was cooled using liquid nitrogen.

CO_2 and NH_3-chemisorption and TPD analyses were performed under He flow rate at 40 mL min^{-1} using a Pulse ChemiSorb2750 Micromeritics instrument. Samples were pre-treated under N_2 at 20 mL min^{-1} flow and 773 K. The ratio strong basic to strong acid sites was determined on the basis of the amount of carbon dioxide and ammonia desorbed during TPD experiments between 473 and 773 K. (Fig. 7) The ratio of strong basic to acid sites was calculated considering the area relevant to desorbed CO_2 and NH_3 in the temperature interval 473–773 K (Eqs. (3) and (4)). The gas evolved below 473 is considered to give weak–medium interactions with the catalyst.

$$\text{Strong basic sites} = \left[\frac{\text{Area } CO_{2\,(473-773K)}}{\text{Area } CO_{2(298-773K)}}\right] \times \text{Total } CO_2 \text{ Adsorbed (mL/g)} \quad (3)$$

$$\text{Strong acid sites} = \left[\frac{\text{Area } NH_{3\,(473-773K)}}{\text{Area } NH_{3\,(298-773K)}}\right] \times \text{Total } NH_3 \text{ Adsorbed (mL/g)} \quad (4)$$

2.1. Synthesis of the catalysts

The notation [xM′O/M″O] is used for the mixed oxides, where *x* indicates the molar ratio of M′ to M″ taken as one.

2.1.1. Synthesis of $2CaO/CeO_2$

$CaCO_3$ (1.32 g) and $Ce(NO_3)_3\cdot 6H_2O$ (2.85 g) were mixed at the solid state using HEM. At the end of the milling (30 min at 700 rpm) the mixture was calcined for 3 h at 823 K.

2.1.2. Synthesis of $0.03Nb_2O_5/CeO_2$

a) To 7 g of $Ce(NO_3)_6(NH_4)_2$ dissolved in anhydrous ethanol (30 mL), 95 μL of $[Nb(OEt)_5]_2$ dissolved in 1 mL of EtOH were added dropwise, keeping the mixture under stirring. A $NH_{3(aq)}$ solution in water (1:10 v/v) was added dropwise until pH 9 was reached. During the addition of the base the precipitation of the hydroxides took place and the solution color changed from red to yellow and finally to pinkish. The suspension was left under stirring for 2 h and then it was centrifuged. The separated hydroxides were washed with water (3 × 5 mL), dried at 503 K for 12 h and, then, calcined at 823 K for 2 h in air.

b) 2 g of CeO_2 and 0.1 g of Nb_2O_5 were ground for 30 min by HEM at a rate of 700 rpm, reversing the rotation of the agata balls every 10 min. At the end of this process, the solid was calcined at 823 K for 3 h.

2.1.3. Synthesis of xMgO/ZnO

*x*MgO/ZnO mixed oxides with $x = 1$; 0.5 were prepared by HEM. $Zn(NO_3)_2\cdot 6H_2O$ (2.02 g) was mixed with 1.73 or 0.88 g of $Mg(NO_3)_2\cdot 6H_2O$ in an agate reactor for 30 min. The obtained solids were calcined at 823 K for 3 h.

2.1.4. Synthesis of ZrO_2/CeO_2

ZrO_2/CeO_2 was prepared by HEM. 1 g of ZrO_2 and 1.4 g of CeO_2 were mixed in an agata reactor and ground for 30 min at a rate of 700 rpm, reversing the rotation of the agata balls every 10 min. At the end of this process, the solid was calcined at 823 K for 3 h.

2.2. Transesterification of DMC with n-butanol

The reaction was carried out in a stainless steel autoclave at 463 K for 12 h using a DMC/^{n}BuOH molar ratio of 1:4. The conversion was followed by GC. When DMC was completely converted, the D^nBC was separated by double distillation. It had purity higher than 99% (elemental analyses and GC–MS) and was suited to be used for building a gas-chromatographic calibration curve.

2.3. Direct carboxylation of n-butanol

2.3.1. Reaction of n-butanol with CO_2

The reaction was carried out in a 100 mL stainless steel autoclave charged with 5 MPa of carbon dioxide. In a typical catalytic test 0.1 g of catalyst were added to 4 mL of *n*-butanol. The reaction was carried out at 433 K for 6 h or, alternatively, as specified. The working pressure reached during the reaction was about 6 MPa. The yield in D^nBC was determined gas-chromatographically using *n*-tridecane as internal standard and expressed either as % D^nBC or as % conversion of butanol (Fig. 1).

2.3.2. Water elimination using CH_3CN

To the reaction mixture as in Section 2.3.1, CH_3CN was added as specified in Table 2. The conversion of *n*-butanol was almost doubled using an excess of CH_3CN, but the reaction mixture was much more complex as by-products are formed as discussed below.

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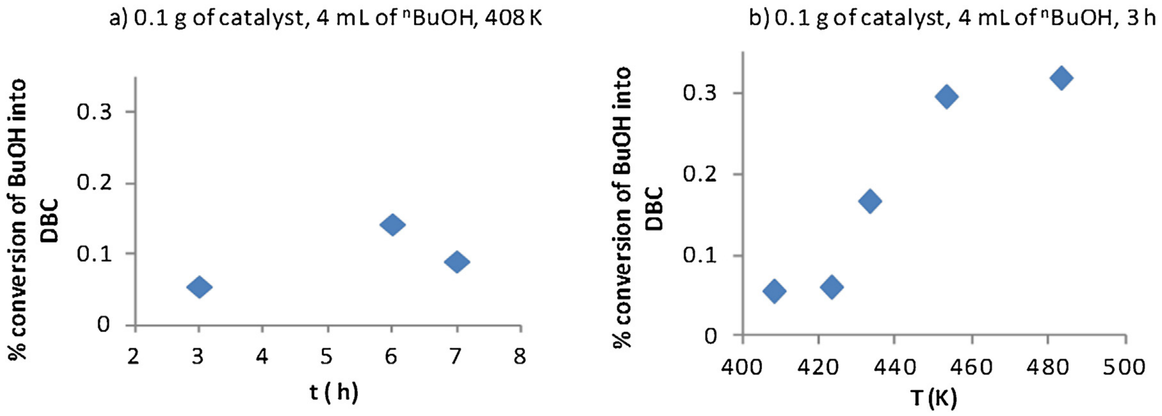

Fig. 1. ^{n}BuOH conversion into D^{n}BC: dependence from time (a) and temperature (b).

2.3.3. *Direct carboxylation of* n-*butanol coupled to pervaporation*

A Na-type pervaporation ceramic membrane (Sulzer) was located in a stainless steel housing covered with a heating ribbon set at 403 K. A Speck pump was used to circulate the feed through the membrane at about 300 mL/min. The permeate was collected in a cold trap. The vacuum pump applied to the permeate produced a final pressure of 10^{-4} MPa.

The catalytic reaction was carried out as reported in Section 2.3. Then it was circulated inside the pervaporation equipment in order to reduce the water content until 100–150 ppm. The dehydrated retentate was used in a new carboxylation run.

2.4. *Butanolyisis of urea*

2.4.1. *Butanolyisis of urea in a closed batch reactor*

The reaction was carried out in a 100 mL stainless steel autoclave connected to a pressure regulation valve through a ~35 cm long stainless steel tube used as refrigerant. In a typical run, 0.5 g of urea were added to 7.6 mL of alcohol (molar ratio alcohol/urea = 10) and 70 mg of catalyst (weight ratio urea/catalyst = 7). The reaction was carried out for 7 h, or as specified. When the working pressure reached 1 MPa, the valve was open and NH_3 was allowed to escape and was collected. As the reaction progressed, a lowering of the pressure was observed due to the lower amount of NH_3 released.

After the autoclave was cooled to room temperature, the reaction mixture was analysed by GC and GC–MS. The yield in D^{n}BC is expressed with respect to urea (the limiting reagent).

2.4.2. *Butanolyisis of urea with intermediate total elimination of NH_3*

The reaction was performed as reported in Section 2.4.1 up to 7 h. The reactor was, then, cooled down to room temperature and opened in order to allow a complete removal of NH_3. The reactor was closed and heated again to 453 K and the reaction continued for the specified time (see Fig. 6).

3. Results and discussion

3.1. *Synthesis of D^{n}BC* via *direct carboxylation of ^{n}butanol*

Our previous studies [20d] on the synthesis of diethyl carbonate *via* the direct carboxylation of ethanol demonstrated the higher catalytic activity of $0.03Nb_2O_5/CeO_2$ with respect to both the pure components and other mixed oxides reported in the literature. $0.03Nb_2O_5/CeO_2$ was used as catalyst in the carboxyation of *n*-butanol starting with the same operative conditions used in the case of ethanol (0.1 g of catalyst, 4 mL of ROH, 408 K, 3 h). It is worth to note that the carboxylation of butanol is slower than that of ethanol using the same operative conditions and the same catalyst [20d]. Several factors could affect such result such as the solubility of CO_2 in the alcohol, the viscosity of the medium and, essentially, the acidity of the alcohol.

The dependence of the D^{n}BC yield on time and temperature is reported in Fig. 1. The best yield of D^{n}BC is observed after 6 h. Increasing the temperature above 433 K, new products are formed. At 453 and 483 K butyraldehyde and butyraldehyde dibutyl acetal were formed together with dibutyl carbonate and the selectivity toward the latter decreases from 100% at 433 K to 55% at 483 K. This makes more complex the separation process and requires a higher energy expenditure in post reaction treatment.

The new species identified in the reaction mixture are products of oxidation of butanol. The latter reaction occurs at expenses of the mixed oxides (Scheme 1), which are reduced to a lower oxidation state or even to metals, which do show a reduced catalytic activity. However, a second negative aspect linked to a higher reaction temperature is the loss of the catalysts.

The best operative conditions in terms of yield and selectivity are, thus, 433 K and 6 h. Other catalysts were tested in such conditions, as reported in Table 1.

$0.03Nb_2O_5/CeO_2$ was synthesized in two different ways (by co-precipitation, Entry 1; or by HEM, Entry 2) in order to verify if the synthetic methodology could affect the catalytic performance.

The two catalysts are almost equivalent, with a very slight higher carbonate yield (0.32 *vs* 0.29%) obtained using $0.03Nb_2O_5/CeO_2$ synthesized by co-precipitation. The difference can be due to the

Table 1
D^{n}BC synthesis by carboxylation of ^{n}BuOH using different mixed oxides. (Operative conditions: BuOH = 4 mL, P = 5 MPa of CO_2, T = 433 K, t = 6 h, 100 mg of catalyst).

Entry	Catalyst	Conv. of ^{n}BuOH into D^{n}BC [%]
1	$0.03Nb_2O_5/CeO_2$ coprecip	0.32
2	$0.03Nb_2O_5/CeO_2$HEM	0.29
4	ZrO_2/CeO_2	0.3
3	0.5MgO/ZnO	0
7	ZrO_2	0.03
5	La_2O_3	0
6	TiO_2	0

Table 2
Direct carboxylation of *n*-butanol catalysed by $0.03Nb_2O_5/CeO_2$ in presence of CH_3CN as dehydrating agent.

Entry	Reaction conditions	Conv. of ^{n}BuOH into D^{n}BC [%]
1	T = 433 K, 6 h	0.32
2	T = 433 K, 6 h, CH_3CN:BuOH = 1:1	0.5
3	T = 433 K, 6 h, CH_3CN:BuOH = 2:1	0.56
4	T = 433 K, 20 h, CH_3CN:BuOH = 2:1	0.59

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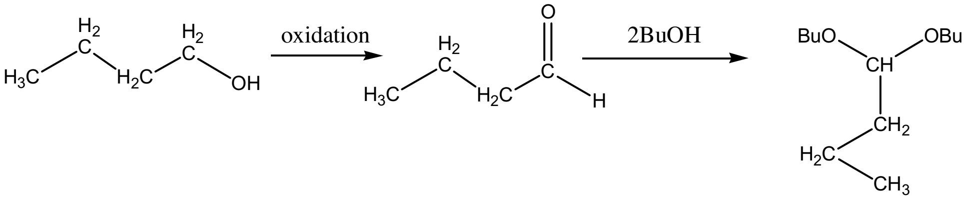
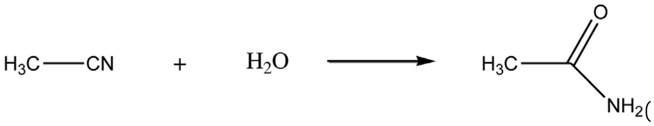


Scheme 1. Formation of butyraldehyde and butyraldehyde dibutyl acetal from BuOH.

higher surface area of particles formed using the coprecipitation method with respect to HEM [37].

In order to try to increase the D^{n}BC yield, acetonitrile was added as an organic water-trap to overcome the thermodynamic limitations of the reaction. (Table 2) [21]. It is worth to note that CH$_3$CN, while improving the conversion of butanol, causes the formation of several products such as acetamide-AA (Eq. (5)), butyl acetate-BA (Eq. (6)) and trace of butyl carbamate-BC (Eq. (7)) as revealed by GC–MS analyses, making more difficult and energetically more demanding the recovery of the target product.

Using an excess of acetonitrile for long time of reaction (Table 2, Entry 4) the D^{n}BC yield was almost doubled with respect to the case in which it was absent (Entry 1). But, concurrently, also the formation of BA and BC was largely observed.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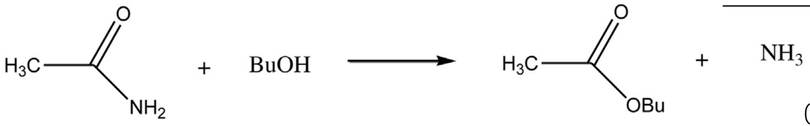
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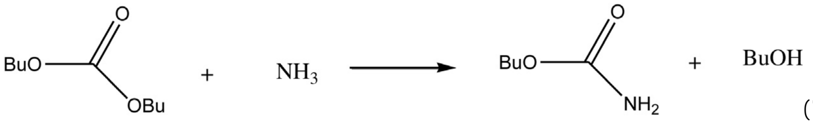
(7)

Despite the positive effect on the formation of D^{n}BC, the fact that the selectivity is lowered, does not make such methodology a winning option [38] also because the hydrated form of the water trap must be dehydrated and the water trap re-circulated, in order to reduce waste formation. Therefore, we have used a pervaporation membrane for the elimination of water. Under such circumstances the conversion of butanol was raised up to 0.55% after only one "carboxylation–pervaporation–carboxylation" cycle without production of co-products. The membrane is enough selective toward water: 9.8% butanol and 3.9% D^{n}BC were lost with the permeate. Moreover, the membrane does not need any activation after use. Such technique seems to be more suited for boosting the production of D^{n}BC from butanol and CO$_2$, than the addition of chemical traps, although the total conversion remains modest.

3.2. Synthesis of D^{n}BC via *^{n}Butanolysis of urea*

The butanolysis of urea was performed by testing several different mixed oxides, which may be characterized by having either intermediate acid-base properties with respect to single oxides or even show quite different features. We have combined metals with strong acid (Nb), basic (Ca, Mg) or intermediate acid-base (Zn, Ce) properties in order to identify which of them were more suitable for the butanolysis of urea. The recoverability and recyclability of the most interesting catalysts were also studied as such properties have key importance for up-scaling and exploitation of the synthetic methodology. In Table 3, the activity of the tested catalystsis reported and expressed as conversion of urea into D^{n}BC. The corresponding pure oxides have been also tested for comparison.

Table 3
D^{n}BC synthesis by butanolysis of urea using different pure and mixed oxides. (Operative conditions: BuOH = 8 mL, T = 453 K, t = 7 h, 70 mg of catalyst).

Entry	Catalyst	Strong basic/strong acid sites (n_B/n_A)	D^{n}BC yield [%]
1	ZnO	0.9	9.1
2	MgO	1.2	7.5
3	CaO	2.7	7.4
4	CeO$_2$	0.75 [20d]	3.6
5	2CaO/CeO$_2$	2.47 [36]	10.0
6	0.5MgO/ZnO	1 [36]	8.8
7	MgO/ZnO	0.8	3.5
8	0.03Nb$_2$O$_5$/CeO$_2$	0.45 [20d]	5.7

Under the reaction conditions, similar to those used in the ethanolysis of urea in our previous works [36,39], the most active catalyst results to be 2CaO/CeO$_2$ (Table 3, Entry 5), despite of the moderate activity of the relative pure oxides CaO and CeO$_2$ (Entries 3 and 4).

Its activity is higher than that of ZnO. Table 4 compares the activity of most active catalysts in three consecutive runs. The slight deactivation observed for 2CaO/CeO$_2$ (Table 4, Entry 1) is due to a only partial conversion of CaO into CaCO$_3$.

This is confirmed by FTIR spectra (Fig. 2) of the solids recovered at the end of the reaction (a signal at 1754 cm^{-1} due to carbonate moiety is quite evident). By calcining the solid before re-use CaCO$_3$ is converted back to CaO and the catalyst retains its performance as already observed in the ethanolysis of urea [36].

Table 4
Study of recyclability of the catalyst. (Operative conditions: BuOH = 8 mL, T = 453 K, t = 7 h, 70 mg of catalyst).

Entry	Catalyst	D^{n}BC yield I cycle [%]	D^{n}BC yield II cycle [%]	D^{n}BC yield III cycle [%]
1	2CaO/CeO$_2$[a]	10	8.9	7.5
2	ZnO[a]	9.1	18.4	5.6
3	ZnO$_{calc}$[b]	9.1	7.4	8.4
4	0.5MgO/ZnO[a]	8.8	9.2	9.4
5	0.5MgO/ZnO$_{calc}$[b]	8.8	13.8	12.9

[a] The catalyst was separated from the liquid phase by centrifugation, dried under vacuum and used in the following cycle.
[b] The catalyst was calcined before its re-use in catalysis.

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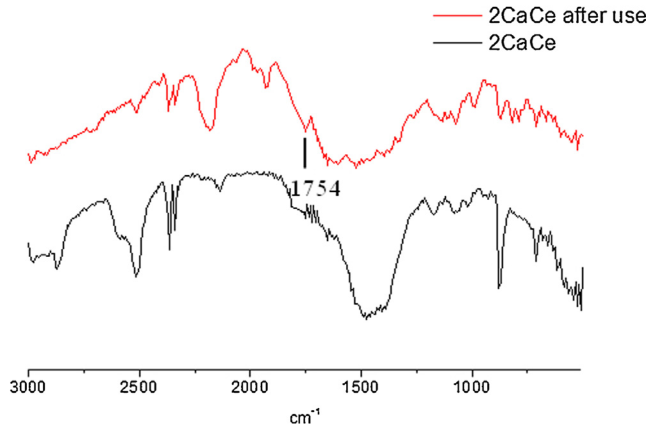

Fig. 2. FTIR spectra of $2CaO/CeO_2$ mixed oxide after three consecutive reaction cycles.

Table 5
Leaching of the metal centre in three consecutive cycles of reaction.

Catalyst	Leached metal	I cycle	II cycle	III cycle
$2CaO/CeO_2$	% Ca	1.2	0.27	0.8
	% Ce	0.4	1.6	0.25
ZnO	% Zn	1.54	0.15	0.9
0.5MgO/ZnO	%Zn	0.36	1.95	3.65

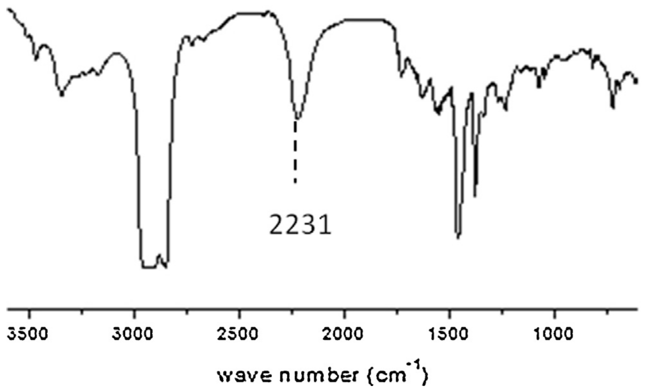

Fig. 3. FTIR spectrum of ZnO after use in the first catalytic cycle: the band at 2231 cm^{-1} is attributed to bound NCO.

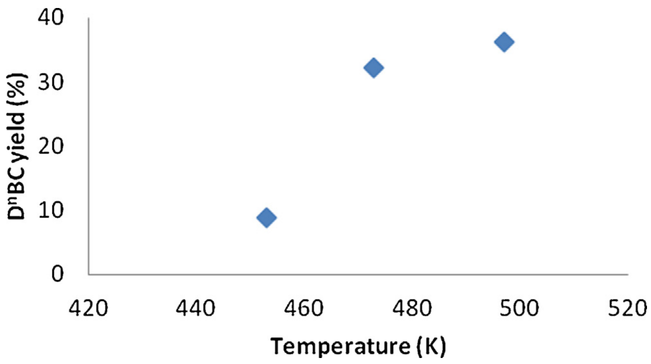

Fig. 4. Effect of reaction temperature on D^nBC yield. (^nBuOH/urea molar ratio = 10: urea/catalyst ratio (w/w) = 7, time = 7 h, catalyst: 0.5MgOZnO).

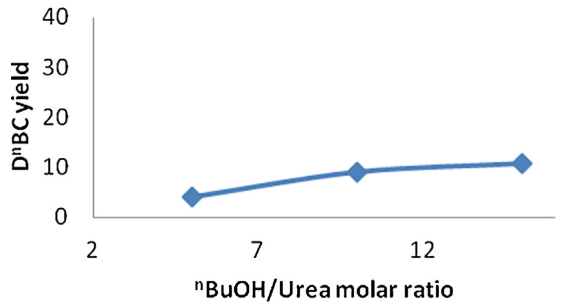

Fig. 5. Effect of ^nBuOH/urea molar ratio on D^nBC yield (urea/catalyst ratio (w/w) = 7:1, T = 453 K, time = 7 h, catalyst: 0.5MgO/ZnO).

Under the operative conditions, the catalysts do not undergo significant leaching, (Table 5) and reveal to behave as real heterogeneous catalysts.

$0.03Nb_2O_5/CeO_2$, the most acid catalyst among those reported in Table 3 [20d], does not show a satisfying catalytic performance (Table 3, Entry 8), confirming the literature data that say that catalysts with strong acidity, such as Al_2O_3 and ZrO_2, are worst than basic catalysts such as CaO, MgO and La_2O_3 [35] in the alcoholysis of urea.

Using ZnO (Table 3, Entry 1) and 0.5MgO/ZnO mixed oxide (Table 3, Entry 6) almost the same D^nBC yield was obtained but the recyclability of the two catalyst shows a different behavior. (Table 4, Entries 2–5)

ZnO shows an irregular trend over three reaction cycles: its catalytic activity increases after the first reaction cycle, and decreases in the third one. (Table 4, Entry 2) If the solid is calcined at the end of each cycle such irregular trend is no more observed (Table 4, Entry 3).

As reported in the literature [39,40], ZnO is prone to form homogenous coordination complexes such as $Zn(NCO)_2(NH_3)_2$ with ammonia and isocyanate (Eq. (9)) formed upon decomposition of urea at high temperature (above 435 K, Eq. (8)). The homogeneous catalyst has been shown to be the active species and can be lost with the liquid phase in the case of ethanol [40c] in which it is soluble.

$$(H_2N)_2CO \rightarrow NH_3 + HNCO \quad (8)$$

$$ZnO + 2HNCO + 2NH_3 \rightarrow Zn(NCO)_2(NH_3)_2 + H_2O \quad (9)$$

Conversely, in the butanolysis of urea $Zn(NCO)_2(NH_3)_2$ is formed, as demonstrated by FTIR spectrum (Fig. 3), but it shows a low solubility in the reaction medium as confirmed by the EDX data (Table 5). Therefore, because the active species is not lost in the liquid phase and remains in the solid separated from the reaction mixture, it is prompt to act as catalyst in the second run without any induction time, producing a higher carbonate yield. The reason of the deactivation of the catalyst in the third cycle is still under investigation. FTIR spectra suggest that $Zn(NCO)_2(NH_3)_2$ can be converted in other species not yet identified but not active in catalysis.

In order to fully elucidate the behavior of ZnO, we have carried out the butanolysis of urea in presence of fresh ZnO for different reaction times, longer than 7 h: a higher yield of carbonate was found (D^nBC yield about 23.2%) after 14 h.

0.5MgO/ZnO, differently from all the other mixed oxides, retains about the same catalytic activity in three consecutive cycles even if the catalyst is re-used without calcination. (Table 4, Entries 4–5) This suggests that the nature of the catalyst does not change during catalysis. It was, then, used in the investigation of the effect of further reaction parameters.

The results of a study on the influence of the temperature on the final yield is shown in Fig. 4. Increasing the temperature up to 497 K, the D^nBC yield increases.

At higher reaction temperature, the carbonate yield reaches really interesting values (32.1 and 36.2% at 473 and 497 K respec-

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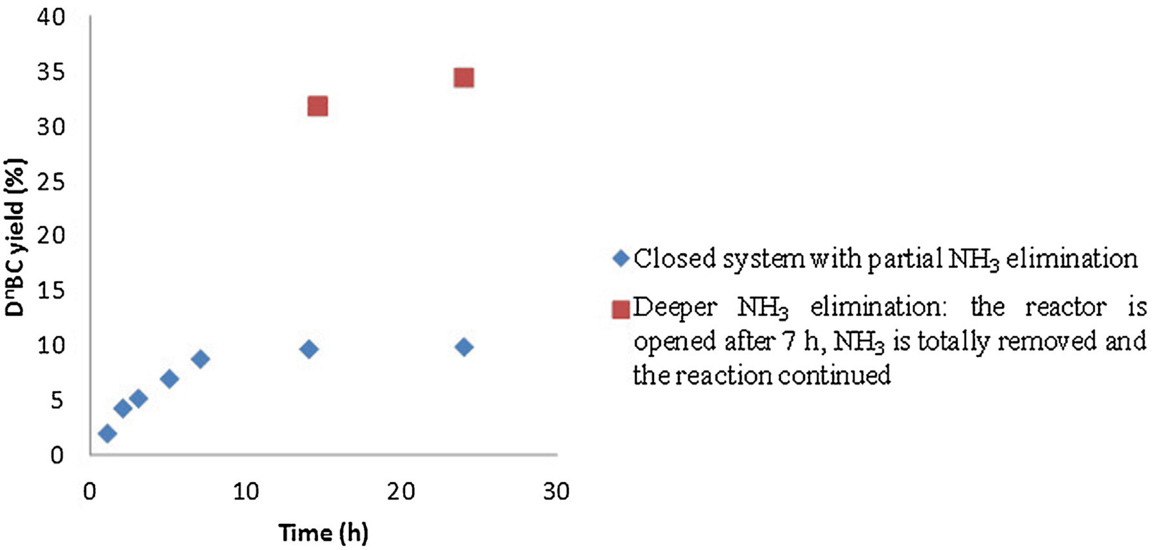

Fig. 6. Trend of D^{n}BC yield (%) *vs* reaction time (*h*) in presence of 0.5MgO/ZnO mixed oxide as catalyst using different reaction conditions. (Urea/catalyst w/w ratio = 7:1, *T* = 453 k).

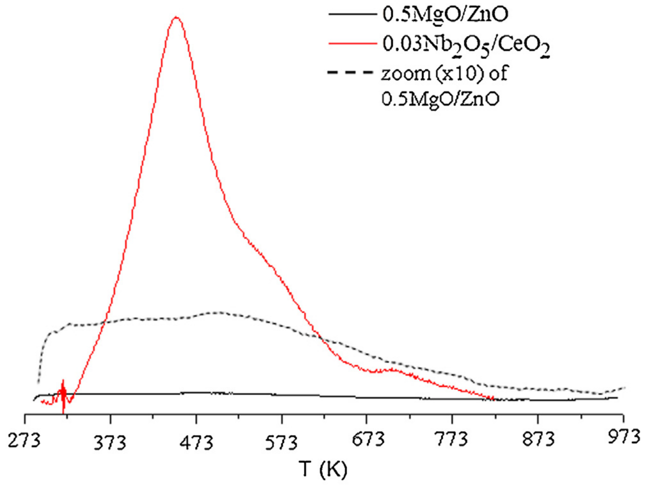

Fig. 7. NH_3-TPD profiles of 0.5MgO/ZnO and $0.03Nb_2O_5/CeO_2$ catalysts [20d,36].

tively) but increasing amounts of by-products are formed. GC–MS analysis on the liquid phase reveals the presence of butyraldehyde dibutyl acetal and *N*-butyl butylcarbamate (*N*-BBC). The first could be formed from the oxidation of butanol as also observed in the direct carboxylation. *N*-Butyl butylcarbamate (*N*-BBC) comes from the akylation of butylcarbamate by butylcarbonate. Therefore, the increased conversion of butanol is accompanied by a loss of selectivity, not a good feature, and decomposition of catalysts.

The effect of butanol/urea initial molar ratio on D^{n}BC yield is shown in Fig. 5. Increasing the ^{n}BuOH/urea molar ratio from 5:1 to 10:1 there is an increase in D^{n}BC yield from 4 to 8.8%. However a further increase of the alcohol does not produce a further significant increase of the carbonate yield which is 8.8 and 10.9% at 10:1 and 15:1 ^{n}butanol/urea molar ratio, respectively. So the molar ratio 10:1 seems to be the best to use.

A kinetic study of the reaction catalysed by 0.5MgO/ZnO (Fig. 6) carried out in the best operative conditions in a closed vessel shows that the rate of carbonate production increases quite linearly up to 7 h and then reaches a pseudo-equilibrium (D^{n}BC yield = 10% conversion). A different trend is observed when the reaction is carried out with a more efficient NH_3 elimination: in such conditions higher D^{n}BC yields can be reached at longer reaction times: 32.0% and 34.5% after 14 and 24 h respectively, since removing ammonia from the reaction medium allows to shift the equilibrium to right [36].

In conclusion, the best conversion yield of urea (>35%) is observed at 497 K, working with a BuOH/urea molar ratio equal to 10, and carrying out the reaction for 7 h, upon continuous NH_3 removal by bubbling N_2 with strict butanol recovery [41].

3.3. Comparison between alcoholysis of urea and direct carboxylation of n-butanol

By comparing the results obtained with the butanolysis of urea and the direct carboxylation of butanol for the synthesis of *n*-butyl carbonate two important aspects can be highlighted:

1) The two routes afford quite different yields of D^{n}BC, the butanolysis of urea being more efficient. Even using a dehydrating agent, the yield in carbonate obtained in the direct carboxylation process is close to two orders of magnitude lower than that obtained through the alcoholysis of urea. This can be explained by the higher stability and lower reactivity of the CO_2 molecule with respect to urea, and the relevant thermodynamic constraints.
2) The same catalysts show completely different activity in the two processes. In fact, the most active catalyst for the butanolysis of urea, namely 0.5MgO/ZnO, is not active in the direct carboxylation of butanol, in which catalysts like $0.03Nb_2O_5/CeO_2$ perform much better. It is worth to underline that the latter shows a poor activity in the alcoholysis of urea. The explanation of such behavior can be found in the different reaction mechanisms of the two processes. (Scheme 2).

Looking at the reaction mechanisms reported in the literature [20c,d,42], it is possible to note that the role of the basic sites is the same in the two processes: they interact with the alcohol molecule to form the alcoholate moiety. The main difference is in the role of the acid sites since in pathway A they interact with alcohol to form the alkyl cation, whereas in path B they coordinate carbamate to favor the nucleophylic attack of the alcoholate.

If NH_3-TPD profiles of $0.03Nb_2O_5/CeO_2$ and 0.5MgO/ZnO are compared [20c,36], it is possible to observed that the former has a larger number of acid sites (signal at 450 and 555 K) with respect to the latter that shows only a small amount of strong acid sites

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Path A	Path B
$ROH + B \rightarrow RO^- + BH^+$	$ROH + B \rightarrow RO^- + BH^+$
$RO^- + CO_2 \rightarrow ROCOO^-$	$(NH_2)_2CO + ROH \xrightarrow{\Delta} NH_2COOR + NH_3$
$ROH + A \rightarrow R^+ + AOH^-$	$NH_2COOR + A \rightarrow (NH_2)(OR)CO \cdots A$
$R^+ + RCOO^- \rightarrow ROCOOR$	$RO^- + (NH_2)(OR)CO \cdots A \rightarrow ROCOOR + ANH_2^-$
	$ANH_2^- + BH^+ = A + B + NH_3$

Scheme 2. Putative reaction pathway for (A) direct carboxylation of alcohols, (B) alcoholysis of urea.

(at 485 K). Such different acid properties agree with the different behavior of the two catalysts in the direct carboxylation and butanolysis of urea.

4. Conclusions

Di-*n*-butyl carbonate (D^nBC) was synthesized reacting ^{n}butanol with either CO_2 or urea. Catalysts with different acid/basic properties are required in the two synthetic methodologies.

The direct carboxylation of *n*-butanol is favored by more acid catalysts such as $0.03Nb_2O_5/CeO_2$ and by water elimination. However, even if it is the most interesting route for the synthesis of carbonates thanks to the simplicity of the process, the obtainable D^nBC yields are always lower than that obtained by the butanolysis of urea, an indirect route to use CO_2.

On the other hand, basic catalysts are required for the butanolysis of urea. $2CaO/CeO_2$ results to be the most active catalyst in the first cycle of reaction, whereas the 0.5MgO/ZnO is the most robust since its catalytic activity is approximately the same during three consecutive catalytic tests both when the catalyst is re-used such as in a next run, or it is calcined before re-use: such mixed-oxide can be easily recycled.

Several reaction parameters were investigated using 0.5MgO/ZnO. It was found that a smaller catalyst amount can ensure a better catalytic performance most probably because the active metal center are employed in the carbonate formation and side reactions are prevented.

A higher reaction temperature leads to an increase in D^nBC yield although it consistently affects the selectivity toward the carbonate.

Using a low BuOH/urea initial molar ratio a lower carbonate concentration is obtained, while increasing the molar ratio higher yields are obtained. The most suited ratio is 10.

The profile of the reaction kinetics points out that the D^nBC yield tends to an equilibrium value at longer reaction time (24 h).

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