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Synthesis of diethylcarbonate by ethanolysis of urea catalysed by heterogeneous mixed oxides

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New Zn- and Ca-based mixed oxides have been tested in the ethanolysis of urea. Cerium and magnesium have revealed to be able to stabilize and enhance the activity of Zn and Ca. All the used compounds act as heterogeneous catalysts in a batch reactor and can be easily recovered and re-used in several catalytic runs. However, although ZnO dissolves as $Zn(NCO)_2(NH_3)_2$ in the reaction medium under the operative conditions and then partly precipitates at room temperature ensuring a modest immediate recoverability and recyclability, $2CaO/CeO_2$ is insoluble also at the reaction temperature that makes it well suited even for the use in a flow reactor. MgO-ZnO and SiO_2-ZnO have also been tested. The former has an interesting performance, but still not equal to that of $2CaO$-CeO_2. Interestingly, the latter catalyst is able to convert urea and ethanol into DEC with 91% conversion of urea and 98% selectivity in the long term.

1. Introduction

Dialkylcarbonates find industrial application as monomers for polymers,[1-2] alkylating and carboxylating agents,[3] reagents in the production of agrochemicals[4] and pharmaceuticals.[5] They are also used in product formulation sectors and more recently they have been proposed as safer and non-toxic octane-boosters.[6] The most important species are the first and the second homologues of the family, namely dimethyl- (DMC) and diethyl-carbonate (DEC), even if dibutyl carbonate is attracting a lot of attention.

Several chemical processes for the synthesis of dialkylcarbonates are known, those on stream are the: i) phosgenation of alcohols,[7] ii) oxidative carbonylation of alcohols (ENIChem[8] and UBE[9] processes), and iii) transesterification of other carbonates.[10] All of them have some drawbacks, such as negative environmental/human health impact (process i), or high risk due to corrosion/explosion (process ii) or even high production costs (process iii which requires another carbonate as starting material). However, new synthetic technologies are required for a large expansion of the market. The direct carboxylation of alcohols,[11] and the alcoholysis of urea are interesting routes from an environmental and economic point of view. The latter even represents an indirect route for CO_2 conversion into chemicals, avoiding the use of toxic chemicals such as phosgene, CO and NO required in conventional dialkylcarbonate production processes and has a more favorable thermodynamics than the direct carboxylation, allowing, thus, to obtain good yields of the target carbonates.[12]

The alcoholysis of urea consists of two steps: first alcohol interacts with urea with a 1:1 molar ratio to give alkylcarbamate (Eq.1), then the latter interacts with a second molecule of alcohol to afford the carbonate. (Eq.2) While Eq. 1 is a thermal process, Eq. 2 is the rate determining step[12a] of the entire process and requires the presence of a catalyst for reaching reasonable conversions.

$$H_2NC(O)NH_2 + ROH \rightarrow H_2NC(O)OR + NH_3 \qquad (1)$$
$$H_2NC(O)OR + ROH \rightarrow (RO)_2CO + NH_3 \qquad (2)$$

In the literature are reported several catalytic systems, most of them are transition metal complexes and behave as homogeneous catalysts.[12-18] ZnO has drawn particular attention thanks to its high catalytic performances.[12,15] It was demonstrated that during the reaction it interacts with the degradation products of urea and converts into the homogeneous complex $Zn(NH_3)_2(NCO)_2$, claimed to be the real active species.[19, 20] (Eq. 3-5).

$$H_2NCONH_2 \rightarrow NH_3 + HNCO \qquad (3)$$
$$ZnO + 2HNCO \rightarrow Zn(NCO)_2 + H_2O \qquad (4)$$
$$Zn(NCO)_2 + 2NH_3 \rightarrow (NH_3)_2Zn(NCO)_2 \qquad (5)$$
$$H_2O + O{=}C(NH_2)_2 \rightarrow NH_4OOCNH_2 \qquad (6)$$

Most of the catalysts reported in the literature are Zn-based compounds in which the active site is the Zn mental centre.[21] Recent studies focus on the discovery of real heterogeneous catalysts,[22a] which allow the use of flow reactors, a very

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important target for the application of such process at the industrial level. We have already investigated the heterogenization of Zn using various frameworks such as mixed oxides, ZIFs and Zn-tethered catalysts, which prevent the solubilisation of the active centre allowing an easy recovery and reuse in other cycles of reaction,[22a] and carried out integrated experimental and computational studies to demonstrate the reaction mechanism.[22b]

Very few studies have been reported in the literature that use metals different from Zn, namely La, Fe or ionic liquids.[23]

Herein we compare the use of ZnO with that of mixed oxides based on Zn or Ca, which show better performance than pure ZnO in terms of reactivity and stability, and are really heterogeneous being not soluble in the reaction medium also under the operative conditions.

2. Results and Discussion

2.1 Catalytic tests and study of the stability of the new catalysts

Si/Zn, Mg/Zn and Ca/Ce mixed oxides with different metal contents were tested in the ethanolysis of urea and compared with the already known ZnO. The obtained results are collected in Table 1 (the catalytic performance of ZnO is reported as benchmark). For each couple of metals, the influence of the chemical composition on the catalytic activity was studied in order to identify the real active metal centre. The 7 h time limit does not correspond to an equilibrium position, as explained in the follow-up of the text. In the case of $xCaO/CeO_2$ mixed oxides it was observed that by changing the molar ratio Ca/Ce in the range $0.2 < x < 2$, the activity of the catalyst increases with the increase of Ca content suggesting that Ca plays a key role in catalysis. The best result was obtained using a molar ratio equal to 2:1 (Ca:Ce) with which a DEC yield comparable to ZnO is obtained. (Tab. 1, Entries 1 and 4)

Moreover, using $2CaO/CeO_2$ mixed oxide the leaching of the active centre in the liquid phase is very low so that the catalyst can be recovered by simple filtration almost quantitatively. (Tab. 2) The activity in catalysis of xMgO/ZnO with $0.1 < x < 2$ (where x represents the molar ratio Mg/Zn) seems to be not so linear with the composition, showing a wave behaviour. The best combination resulted to be 0.5 of Mg and 1 of Zn. (Entry 6). EDX analyses on the liquid phase (Tab. 2) reveal a very low leaching of Zn, making the use of such catalyst more advantageous with respect to ZnO, since it shows even better catalytic performance (Tab.1, Entries 1 and 6) coupled to a higher stability and easier recoverability. The performance of Si/Zn mixed oxides in catalysis is strongly correlated to the Zn content: increasing the Zn/Si molar ratio from 0.05 to 0.5 the DEC yield passed from 0.3 % to 5.5 % demonstrating that the Zn is the active species. The role of SiO_2 is most probably that of stabilizing the catalyst and reducing the leaching of Zn with respect to ZnO. (Tab. 2) In an attempt to further stabilize the Zn centres we have investigated the role of the calcination temperature during the synthetic procedure, by varying it within the range 823-1073 K. The FTIR spectra of the catalyst synthesized at 1023 K show thinner and more resolved peaks in the range 895-940 cm^{-1} with respect to the spectrum of the catalyst synthesized at 823 K. This could be due to structural modifications and in particular to the presence of Si-O bonds of different nature.[24] The catalyst calcined at 1073 K was less active during the first cycle with respect to that calcined at 823 K (Tab. 1, Entries 10,11), but the amount of Zn leached was slightly reduced. (Tab. 2)

Table 1. Yield of DEC produced from Urea and ethanol. (~0.5 g of urea, 5 mL of EtOH, ~70 mg of catalyst, 453 K, 7 h).

Entry	Catalyst	% DEC yield	DEC /M centre [mol/mol]
1	ZnO	18	1.92
2	$0.2CaO/CeO_2$	1.4	0.3
3	CaO/CeO_2	4.2	1.1
4	$2CaO/CeO_2$	18	6.1
5	0.1MgO/ZnO	5.1	0.5
6	0.5MgO/ZnO	18.8	2.26
7	2MgO/ZnO	12.8	2.5
8	$0.05ZnO/SiO_2$	0.3	0.45
9	$0.1ZnO/SiO_2$	1.2	1.04
10	$0.5ZnO/SiO_2$_823	5.5	1.31
11	$0.5ZnO/SiO_2$_1073	3	0.71

Table 2. Distribution of the catalytically active centre between the solid and the liquid phase after use in the ethanolysis of urea (Batch reactor, Urea:EtOH = 1:10, catalyst = 70 mg, temperature = 453 K, time = 7 h)

Sample	% of Zn				% of Ca
	ZnO	0.5Mg/Zn	0.5Zn/Si_823	0.5Zn/Si_1073	2Ca/Ce
Solid phase	0	86	75.2	79	99
Liquid phase	100	14	24.8	21	1

2.2 Study of the recyclability of the catalysts

Thanks to the heterogeneous nature of the tested catalysts, they could be easily recovered and re-used in several cycles of reaction. In Table 3 the DEC yields for three consecutive cycles of reaction are reported per each catalyst.

Table 3. DEC yield respect to urea in three consecutive cycles of reaction using 0.5MgO/ZnO, $2CaO/CeO_2$ and $0.5ZnO/SiO_2$ mixed oxides as catalyst

Entries	**Catalyst**	**% Yield in DEC**		
		I cycle	II cycle	III cycle
1	$0.5ZnO/SiO_2$_823	5.5	4.3	3.6
2	$0.5ZnO/SiO_2$_1073	3	10.6	9.6
3	0.5MgO/ZnO	16	14	14.4
4	$2CaO/CeO_2$	18	7	2.4
5	$2CaO/CeO_2$[a]	18	17.5	17.7

[a] At the end of each cycle, the catalyst has been calcined before its re-use in catalysis

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At the end of each cycle, the reactor was cooled down and the catalyst was recovered by simple filtration and reused such as or after calcination (vide infra). As shown in Table 3, the most stable catalyst was 0.5MgO/ZnO mixed oxide: DEC yield resulted to be about the same in three consecutive cycles of reaction (Tab. 3, Entry 3) with a slight deactivation after the first cycle maybe due to the loss of the 14% of catalyst recorded in the first cycle of reaction. (Tab. 2)

On the other hand, 0.5ZnO/SiO_2 and 2CaO/CeO_2 have shown an irregular trend of DEC yield in three consecutive cycles of reaction. Each case has been studied in detail as reported in the following paragraphs in order to understand the reasons.

2.3 Study of recyclability Zn/Si catalysts

Although 0.5ZnO/SiO_2 calcined at 1073 K seems to be less active during the first cycle than the same catalyst calcined at 823 K, we have observed that in the cycles after the first its activity increased. (Tab. 3, Entry 2) This suggests that during the first cycle the catalyst is in some way activated. Figure 1 compares the FTIR spectra of the catalyst Si/0.5Zn_1073 before and after its use in catalysis when new signals appear. In particular, one can observe new peaks in the range 3430-3173 cm^{-1}, related to N-H stretching, a new signal at 2218 cm^{-1} related to NCO stretching and three new signals at 1705, 1610 and 1553 cm^{-1}, most probably due to different C=O moieties, such as free carbamate, coordinated carbamate and coordinated carbonate. In particular, one finds out the formation of the Zn-isocyanate complex. Therefore, combining the IR data and the leaching results, it is possible to infer that during the catalytic run part of Zn is released from the mixed oxide and converted into the more active Zn-isocyanate species that remains in part entrapped in the silica matrix enhancing, however, the catalytic activity of the solid.

2.4 Study on the recyclability of the 2CaO/CeO_2 catalyst

As described above, 2CaO/CeO_2 works in heterogeneous conditions since it is not soluble in the reaction medium at the reaction temperature and the leaching of calcium in the liquid phase is very low (< 1%). However, the catalyst can be almost quantitatively (>99 %) recovered by simple filtration. (Tab. 2) The only disadvantage is that the considerable catalytic activity during the first cycle seems to be drastically reduced in the following cycles. (Tab. 3, Entry 4)

In order to understand the reasons of such deactivation, detailed studies have been carried out. It was found that the catalyst practically retains its activity if it is calcined before being used in a following catalytic cycle. This suggested that the deactivation was caused by either the absorption of organics on the surface of the starting catalyst or by the conversion of CaO into something less active. Basing on our experience in using Ca-loaded mixed oxides,[25] we supposed that, in presence of water sourced from starting urea, CaO during the reaction could convert into $Ca(OH)_2$ or $CaCO_3$, species not active in the ethanolysis of urea (reactions 7-9).

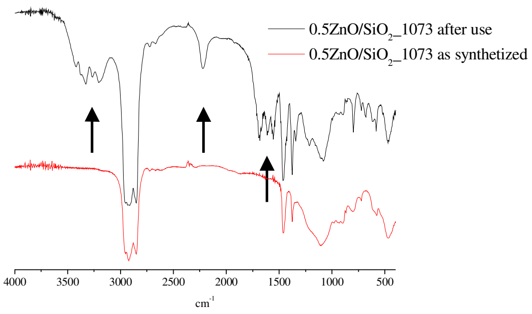

Fig. 1 FTIR spectra of SiO_2/0.5ZnO_1073 before and after the use in catalysis

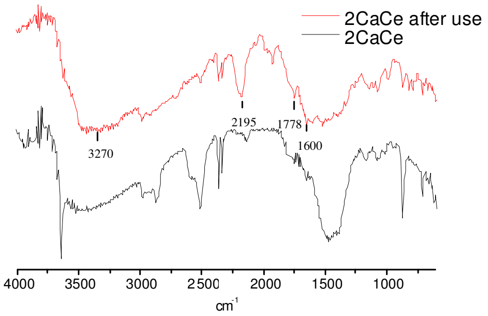

Fig. 2 DRIFT spectra of 2CaO/CeO_2 mixed oxide before and after its use in catalysis

$$HCNO + H_2O \rightarrow CO_2 + NH_3 \qquad (7)$$

$$CaO + CO_2 \rightarrow CaCO_3 \qquad (8)$$

$$CaO + H_2O \rightarrow Ca(OH)_2 \qquad (9)$$

Figure 2 shows the DRIFT spectra recorded on the catalyst before and after the use in catalysis. The spectrum of 2CaO/CeO_2 after its use in catalysis (Fig. 2, red line) revealed the presence of: i) new broad bands at about 1600 cm^{-1} and 3270 cm^{-1}, ascribed to carbamate-species, ii) a band at 2195 cm^{-1} due to the -NCO moiety, and iii) a narrow peak at 1778 cm^{-1}, most probably due to the presence of $CaCO_3$. Such bands were absent in the spectrum of the starting catalyst (Fig. 2, black line). To confirm our hypothesis we have used both Ca-hydroxide and Ca-carbonate in catalysis. Using $Ca(OH)_2$ as catalyst in the ethanolysis of urea, only 1.8 % yield of DEC was obtained. Additionally, the IR spectrum of the catalyst recovered at the end of the reaction revealed that the peak at 3643 cm^{-1}, typical of -OH moiety in $Ca(OH)_2$, had disappeared and a new peak at 1785 cm^{-1} typical of $CaCO_3$ appeared confirming the conversion of $Ca(OH)_2$ into $CaCO_3$ during the reaction. (Fig. 3a)

Similarly, when $CaCO_3$ was used, a DEC yield equal to 2.5 % was obtained. The DRIFT spectrum of the catalyst after use revealed the presence of new broad bands at 1713 and 3150 cm^{-1} due to the presence of ethylcarbamate. The obtained profile was very similar to that of 2CaO/CeO_2 after use in catalysis. (Fig. 3b) The possibility that CaO was converted into $CaCO_3$ during the catalytic run was demonstrated by treating the mixed oxide with wet gaseous CO_2 in EtOH in the operative conditions generally used during the ethanolysis of urea.

At the end of the reaction the solid was analyzed by DRIFT. (Fig. 3c)The obtained spectrum clearly shows the signal at

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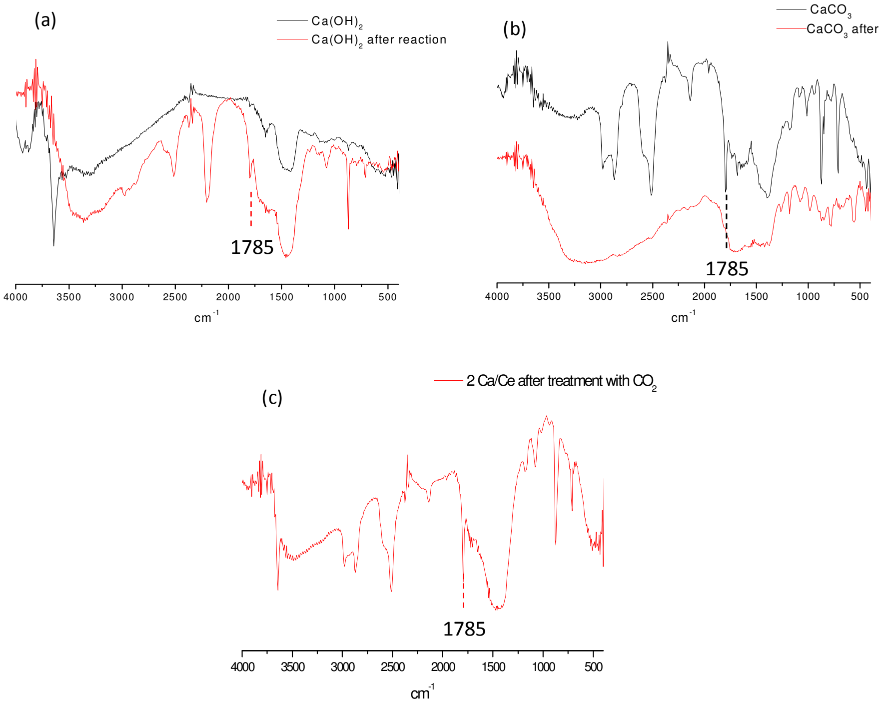

Fig. 3 DRIFT spectra of (a) Ca(OH)$_2$ before and after the use in catalysis; (b) CaCO$_3$ before and after use in catalysis; (c) 2CaO/CeO$_2$ after treatment with CO$_2$

1785 cm^{-1} typical of CaCO$_3$. We have verified that working under anhydrous conditions, the carbonation reaction was much repressed. Therefore, the deactivation of the catalyst could be ascribed to the presence of water that attacks the CaO and converts it into the hydroxide that easily reacts with CO$_2$ produced in reaction 7 and is converted into the carbonate, not active in catalysis.

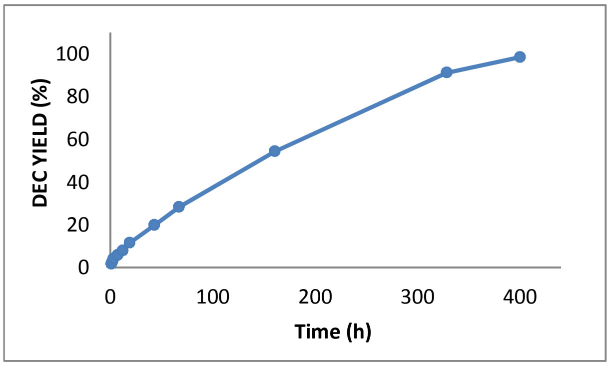

Fig. 4 Kinetics of the ethanolysis of Urea in batch conditions (Batch reactor, Urea:EtOH = 1:10, catalyst = 70 mg, temperature = 453 K)

Such discovery allowed us to avoid the deactivation of the catalyst by using dry urea. Under such conditions we found that, if ammonia is continuously removed from the reaction medium, the ethanolysis of urea proceeds to completion, as demonstrated by the kinetic study in Figure 4: the rate of the reaction slightly decreases after about 20 h but the conversion steadily increases during 320 h (plateau not yet reached in Fig. 4) to afford a DEC yield at this time equal to 91.25 % of the starting urea. In ca. 400 hours the reaction goes to completion (98-99 % conversion) with a very good selectivity (> 98%). After 20 h of reaction some sub-products appear that reach ca 1.5 % after 400 h. The ^{1}H-NMR spectrum of the reaction mixture reveals the presence of several signals in the alkyl region each having a very low intensity and a shoulder to the signal of the NH$_2$- moiety of EC (at 4.9 ppm) that could be due to the n-ethyl ethylcarbamate, the main sub-product formed. The presence of such species was confirmed by the ^{13}C-NMR spectrum along with those of the well established compounds DEC, EC, EtOH. All the other signals were too much low in intensity to have a relevance. Anyway, the calculated integrals in ^{1}H-NMR spectrum indicate that the selectivity towards DEC remains higher than 98% also after a long time of reaction.

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Table 4. BET surface analyses of 0.5ZnO/SiO_2, 0.5MgO/ZnO and 2CaO/CeO_2 mixed oxides

	0.5ZnO/SiO_2	0.5MgO/ZnO	2CaO/CeO_2
BET surface area (m^2/g)	33.95	4.45	6.63

It is clear from the data above that the ethanolysis of urea is not an equilibrium reaction, differently from the direct carboxylation of ethanol that has strong thermodynamic limitations, and is suitable for exploitation.

2.5 Surface characterization of the catalysts

N_2-physisorption experiments were carried out in order to determine the BET surface area of the most active catalysts namely 2CaO/CeO_2, 0.5MgO/ZnO and 0.5ZnO/SiO_2 mixed oxides. (Tab. 4)

0.5ZnO/SiO_2 shows the highest surface area although it is not the most active catalyst. This demonstrates that a high surface area could not ensure high catalytic performances.

Studies on NH_3- and CO_2-Chemisorption followed by TPD have been carried out in order to determine the acid/base properties of the catalysts since, as already demonstrated,[22a] a catalyst with strong acid and basic sites is most suited for promoting the formation of DEC from urea. In fact, basic centres activate the alcohol molecule via abstraction of H^+ while the acid Lewis sites better interact with ethyl carbamate favouring the nucleophilic attack of the alcoholate.

The obtained data confirm such hypotheses. 2CaO/CeO_2, that has revealed to be the most robust and active catalyst, presents both strong basic and acid sites as indicated by the presence of peaks at 659 and 607 K in CO_2- and NH_3-TPD profiles, respectively. (Fig. 5) 0.5MgO/ZnO does not show any strong basic sites but it shows a high number of acid sites of different strength as demonstrated by the very large signal in NH_3-TPD profile that cover all the range from 273 to 823 K. (Fig. 5b) TPD profiles of 0.5ZnO/SiO_2 does not show any strong signals in the region between 573-823 K suggesting that only weak-medium acid and basic sites are present. This confirms that the presence of SiO_2 does not enhance the catalytic activity of Zn, but just makes it more stable and reduces the leaching of the active metal centres in the liquid phase.

2.6 Study of the leaching of the active centre under the operative conditions

The use of a continuous process is a very important target for the ethanolysis of urea so an active and completely insoluble catalyst is required. In order to confirm the heterogeneous nature of the catalysts also in the operative conditions we have set up the equipment depicted in Scheme 1.

A stainless steel tube equipped with an electrical heater (flow reactor) was packed with a known amount of catalyst and heated at the same temperature used in the reaction conducted in batch (453 K). A ethanol solution containing urea (molar ratio EtOH:urea= 10:1) was circulated several times through the column at a flow rate = 0.1 mL/min. After 7 h or reaction, the liquid reaction mixture was separated from the solid and analysed by EDX in order to determine the amount of leached catalyst. Table 5 shows the results for the three catalysts tested. Surprisingly, the percentage of Zn leached in case of 0.5ZnO/SiO_2 is much higher working in the flow reactor with respect to what was found in batch. This suggests that the catalyst has a quite high solubility at the operative temperature (453 K) and precipitates at room temperature. The leaching of Zn using 0.5MgO/ZnO is quite the same in flow conditions as in batch.

Noteworthy, also in the continuous reactor, 2CaO/CeO_2 is the most stable catalyst giving only 1.9 % of leaching of the active metal centre. (Tab. 5)

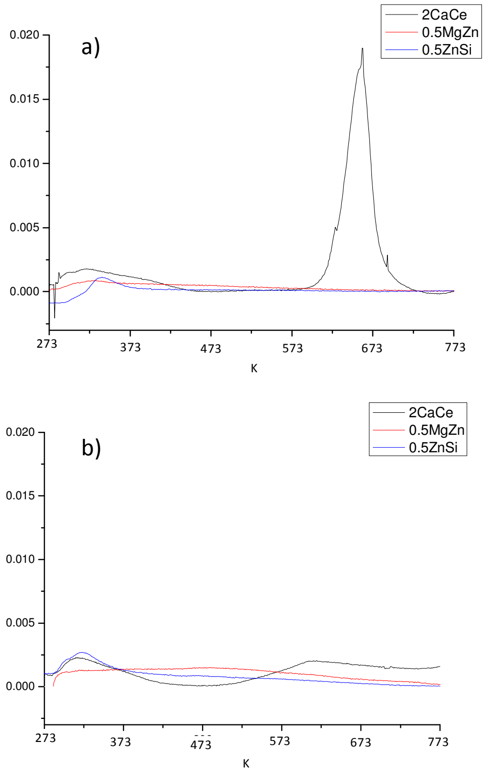
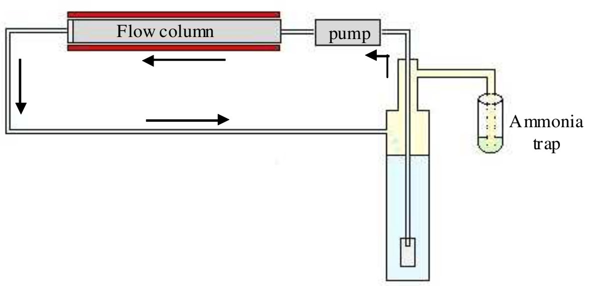


Fig. 5 (a) CO_2 and (b) NH_3-TPD profiles of the catalyst



Scheme 1. Equipment used to test the leaching of the catalysts in a flow-reactor under the following operative conditions: temperature = 453 K, flow rate = 0.1 mL/min, time = 7 h

Table 5. Leaching in the liquid phase of active species of $0.5ZnO/SiO_2$, $0.5MgO/ZnO$ and $2CaO/CeO_2$ mixed oxides in the flow reactor

	$0.5ZnO/SiO_2$	$0.5MgO/ZnO$	$2CaO/CeO_2$
% of active species in the liquid phase	38 % of Zn	15 % of Zn	1.88 % of Ca

The catalyst recovered from the reactor was analyzed by EDX that revealed the presence of more than 90% of starting Ca. The ratio Ca/Ce was equal to 1.9/1 so it remained essentially unchanged during the reaction. On the basis of such study, the most suited catalyst to be used in a flow reactor reveals to be $2CaO/CeO_2$.

Such study also revealed that urea can rise quite a few issues, as its solubility in ethanol strongly depends on the temperature and eventual drops of temperature may cause its crystallization, resulting in the blockage of narrow tubing and valves.

Therefore ethylcarbamate-EC was used in the following study, in order to avoid any solid deposition in the reactor or circuit and sampling valves connected to GC. EC was prepared from ethanol and urea using a thermal route, as mentioned above.

2.7 Use of flow reactor in the conversion of EC into DEC

The equipment working in continuous was set up as reported in Scheme 2. The parameter-space was optimized in order to improve the catalytic activity of the material, maximize the DEC yield and minimize problems of condensation/polymerization of sub-products that usually affect the regularity of the flow rate in the equipment. The following operative conditions were found to be the best: starting feed = 2.8 g of EC in 50 mL of ethanol, flow rate 0.3 mL/min, temperature = 463 K.

The DEC yield (15 % conversion after 7 h) was slightly improved with respect to that obtained in a batch reactor (12 %), but such experiment opens to a continuous production of DEC that we are now pursuing. If the reaction is continued for longer time, as in the case of urea, the complete conversion of EC into DEC can be reached.

3. Experimental

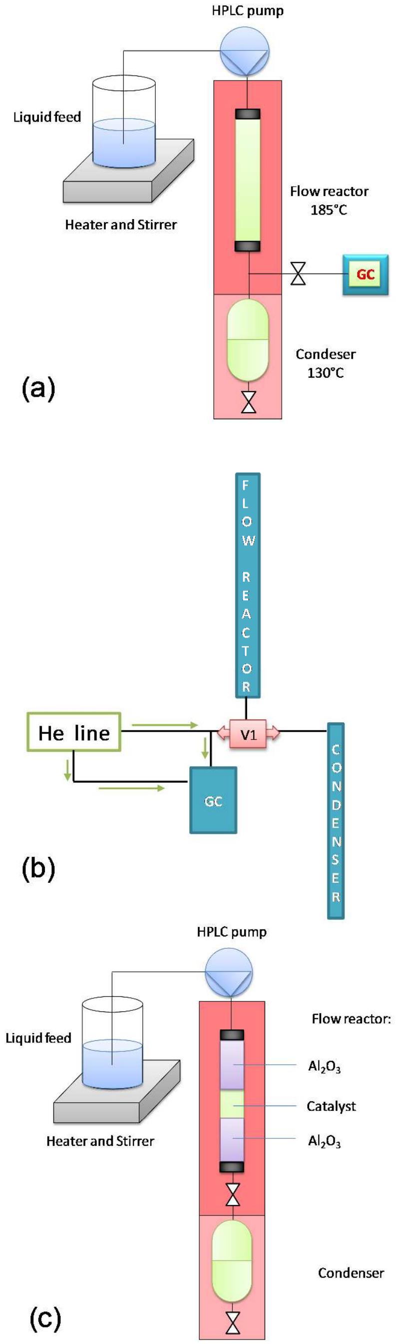
All solvents and reagents were RP Aldrich products. Ethanol was dried, distilled[26] and stored under dinitrogen.

Solid state syntheses were carried out using a Pulverisette 7 Fritsch High Energy Milling at 700 rpm. The obtained solids were then calcinated at the desired temperature.

Liquid state syntheses were carried out using an automatic Zinsser synthesizer.

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

GC-MS analyses were carried out with a gas chromatograph Shimadzu 17 A (capillary column: 30 m; MDN-5S; 1 0.25 mm, 0.25 mm film) coupled to a Shimadzu QP5050 A mass spectrometer.



Scheme 2. Equipment to carry out the ethanolysis of EC in continuous: a) main components of the overall equipment, b) flow reactor-GC connection, c) packing of the flow reactor

Quantitative determinations on the reaction solutions were performed using Hewlett Packard 6850 GC-FID (capillary column Carbowax, 30 m, Ø 0.25 mm).

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FTIR-DRIFT spectra were recorded with a Shimadzu Prestige 21 instrument equipped with the Shimadzu DRS-8000 basic apparatus modified for our purposes.

Surface characterization was done using a Pulse ChemiSorb2750 Micromeritics instrument. The samples were pre-treated under N_2 at 20 mL·min^{-1} flow and 773 K. BET surface analyses were done using 30% N_2/70% He gas mixture. The analyses of the base and acid sites were carried out using CO_2 and NH_3 respectively as probe-gas. The Pulse Chemisorbtion was carried out using He as carrier gas (40 mL min^{-1}). The TPD were performed under He flow at 40 mL min^{-1}.

3.1 Synthesis of mixed oxides

3.1.1 Synthesis of Si/Zn mixed oxides. SiO_2/0.05ZnO, SiO_2/0.1ZnO and SiO_2/0.5ZnO mixed oxides were prepared by mixing 0.2 g, or 0.4 g or 2 g of ZnO, respectively with 3.0 g of SiO_2. The reagents were ground together in a High Energy Milling-HEM equipment for 30 min at 700 rpm and then calcined at 823 K or 1073 K for 3h.

3.1.2 Synthesis of Mg/Zn mixed oxides. 0.1MgO/ZnO, 0.5MgO/ZnO and MgO/0.5ZnO mixed oxides were synthesized by mixing the appropriate volumes of the two mother solutions of $Mg(NO_3)_2·6H_2O$ and $Zn(NO_3)_2·6H_2O$ 1.5·10-6 M and using NH_4OH as co-precipitation reagent. The syntheses were carried out using the parallel Zinsser Sophas synthesizer. After the solutions of the precursors were mixed in the required ratio, an aqueous solution of NH_4OH was added as precipitant agent until pH 8 was reached. The obtained precipitate was isolated using a thermo evaporator centrifuge. At the end, the obtained solids were dried for one night at 403 K and then calcined at 823 K for 3 h.

3.1.3 Synthesis of Ca/Ce mixed oxides. 0.2CaO/CeO_2, CaO/CeO_2 and 2CaO/CeO_2 mixed oxides were synthesized. $CaCO_3$ (0.132 g, 0.66 g and 1.32 g, respectively) and $Ce(NO_3)_3·6H_2O$ (2.85 g) were mixed in the solid state using a HEM apparatus equipped with spheres and basket made of agata. At the end of the milling (1 h at 700 rpm) the mixture was calcined for 3 h at 823 K.[25]

3.2 Synthesis of ethylcarbamate

1 g of urea was added to 15 mL of ethanol. The mixture was transferred in a 100 mL stainless steel autoclave and the mixture was kept under stirring for 7 h at 453 K. At the end of the reaction, excess ethanol was evaporated under vacuum and several extraction (5 x 5 mL of ethyl-ether) were made in order to obtain pure EC. (Yield > 90 %)

3.3 Ethanolysis of urea for diethylcarbonate (DEC) production in batch conditions

The alcoholysis of urea was carried out in a 100 mL stainless steel autoclave equipped with a ~ 35 cm long stainless steel tube equipped with a pressure regulation valve at the exit and used as refrigerant. In a typical catalytic test 0.5 g of urea and 5 mL of ethanol (molar ratio EtOH/urea = 10:1) were reacted in presence of 0.07 g of catalyst (weight ratio urea/catalyst = 7:1). The reaction was carried out at 453 K for 7 h. During the first two hours the inner pressure increased because of the release of NH_3 that escaped the reaction vessel through the upper refrigerant, and was collected. A lowering of the pressure was then observed due to the lower NH_3 release. At the end of the reaction the autoclave was cooled to room temperature and the inner liquid solution recovered and analysed by GC.

3.4 Ethanolysis of ethylcarbamate-EC using a flow reactor

The equipment working in continuous was composed of four main parts: 1. a feed tank; 2. a flow reactor; 3. a GC on-line analyser, and 4. a condenser. (Scheme 2a) The flow reactor was connected through a Swagelok valve (V1) to the sampling valve of a GC in order to analyze the reaction mixture at any time. (Scheme 2b) It was packed with the catalyst by filling in the first 13.2 cm with pure Al_2O_3, the middle part (for 4.8 cm of length) with the catalyst mixed to microbeds, while Al_2O_3 was placed again in the last 9 cm. (Scheme 2c)

In such equipment ethylcarbamate-EC was used, instead of urea, because urea gave problems with plugging the connecting tubes. EC was preliminarily formed by heating ethanol and urea, and then distilled off.

The starting feed containing EC dissolved in ethanol (2.8 g in 50 mL) was placed in a stainless steel autoclave and taken at 333 K under stirring during the entire process. The feed was pumped inside the flow reactor using a HPLC pump at a rate of 0.3 mL/min. The flow reactor consisted of a stainless steel tube (d x L, inner V = 0.4 cm x 27 cm, 13.5 cm3) having at both extremities two filters in order to avoid the loss of the catalyst. It was heated using a heating ribbon. Out of the reactor a two-way valve was placed able to switch the outing feed to the collector or to the GC for analysis.

An AGILENT GC equipped with a FID detector and an automatic sampling valve (GSV) equipped with a 6 μl loop was used for analyses. The circuit <flow equipment-GC> was flushed with helium in order to clean the GSV valve. The collector consisted of a stainless steel tube equipped with an electric heater and a manometer.

4. Conclusions

The newly synthesized Ca/Ce, Mg/Zn and Zn/Si mixed oxides have been tested in the ethanolysis of urea or EC.

Among them the most active catalysts are 2CaO/CeO_2 and 0.5MgO/ZnO that give a DEC yield comparable or even better than that obtained using ZnO, one of the most active catalysts described in the literature until now.

0.5ZnO/SiO_2 mixed oxide converts during the catalysis into a more active species in which Zn is in the form $Zn(NH_3)_2(NCO)_2$ that in batch does not solubilise in the reactive medium and remains entrapped in the silica framework.

The same catalyst in a flow reactor has a worse performance with high leaching of Zn.

The stability of each oxide has been tested both in batch and in flow reactors. Interestingly all the used catalysts have revealed to be very stable in batch with reduced leaching of the active metal centre. The role of the mixed-oxides is that of making

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the catalyst not soluble in ethanol so that they can be easily recovered and reused in consecutive runs. Each of them keeps its activity in several cycles after the first if a completely anhydrous medium is used.

The most suited catalyst to be used in flow conditions is $2CaO/CeO_2$ due to its insolubility in the reaction medium and high stability under anhydrous conditions. The full conversion of urea into DEC is a possible target, as demonstrated by long term kinetics run using $2CaO/CeO_2$.

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