## Ceria nanoparticles as heterogeneous catalyst for $CO_2$ fixation by $\omega$ -aminoalcohols<sup>†</sup>

Raquel Juárez, Patricia Concepción, Avelino Corma\* and Hermenegildo García\*

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In contrast to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, MgO and Y<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub> is a reusable catalyst for the reaction of CO<sub>2</sub> with  $\omega$ -aminoalcohols to form cyclic carbamates; the highest yield (68%) was obtained for the preparation of *N*-alkyl 1,3-oxazolidin-2-ones from *N*-alkyl ethanolamines.

The use of CO<sub>2</sub> as C1 feedstock ("CO<sub>2</sub> *fixation*") replacing methane and CO is a hot topic in Green Chemistry.<sup>1–3</sup> Compounds developed from CO<sub>2</sub> trapping can enjoy the advantage of "CO<sub>2</sub> *neutrality*", minimizing the impact of many chemical syntheses having a positive CO<sub>2</sub> balance.<sup>1</sup>

The main problem in  $CO_2$  fixation reactions is the high thermodynamic stability of  $CO_2$  that renders most of the equilibria unfavorable toward product formation.<sup>4</sup> Alcohols and amines react with  $CO_2$  forming dialkyl carbonates and N,N'-dialkyl ureas that can be used as the starting materials for green alkylations and for the formation of carbamates.<sup>3,5</sup> In the context of new processes for  $CO_2$  fixation and compared to simple alcohols,  $\omega$ -aminoalcohols should react with  $CO_2$ with somewhat more favorable equilibrium toward product formation due to favorable intramolecular trapping of the hydroxyl group of the carbamic acid intermediate leading to the formation of cyclic carbamates (Scheme 1).

The present work describes the activity of ceria as heterogeneous catalyst for the reaction of CO<sub>2</sub> with primary and *N*-substituted  $\omega$ -aminoalcohols. CeO<sub>2</sub> and ZrO<sub>2</sub> are the most widely solid catalysts for various CO<sub>2</sub> fixation reactions.<sup>3,6–8</sup> In a prior study, we found that CeO<sub>2</sub> catalyses transalkylation of propylene carbonate with linear alcohols.<sup>8</sup>

Ethanolamines can react with  $CO_2$  giving rise to the corresponding *N*-alkyl 1,3-oxazolidin-2-ones. Oxazolidinones have a wide range of applications as suitable polar solvents, as synthetic intermediates and chiral inductors.<sup>9–11</sup> The synthesis of these pentacyclic heterocycles can be achieved by direct reaction with  $CO_2$  as indicated in Scheme 1. Analogously, the reaction of 3-aminopropanol and 4-aminobutanol would render 1,3-oxazinan-2-ones and 1,3-oxazepan-2-ones that are useful as reaction intermediates for the synthesis of compounds with biological activity.<sup>12–14</sup>

In the first stage of our work we selected diethanolamine as substrate and performed the screening of a series of metal oxides to promote the  $CO_2$  insertion (Scheme 2). The reason for this selection is that diethanolamine is widely used as solvent to trap CO<sub>2</sub>. Considering transalkylation of organic cyclic carbonates as a related precedent,<sup>8</sup> we selected nanoparticulated metal oxides as solid catalysts, including  $\gamma$ -alumina, P-25 titania, nanoparticulated ZrO<sub>2</sub> (40 nm average particle size), high surface area MgO nanoparticles and Y<sub>2</sub>O<sub>3</sub> nanoparticles. Another series of catalysts were prepared by deposition of Au nanoparticles on nanoparticulated CeO<sub>2</sub>. The catalytic data obtained for oxazolidinone formation from diethanolamine are summarized in Table 1.‡

As it is indicated in Table 1, negative results were obtained in all cases (footnote a), except in the case of ceria. Two samples of ceria differing in the average particle size were tested and it was found that nanoparticulated ceria of 5 nm average size (np-CeO<sub>2</sub>) is most active, but less selective than the commercial non-nanoparticulated ceria sample of larger average particle size, CeO<sub>2</sub> (40 nm). The data of Table 1, showing that yields between 24 and 29% of oxazolidinone can be obtained by reaction with CO<sub>2</sub>, are remarkable and much higher than those obtained for dimethyl carbonate formation by reaction of CH<sub>3</sub>OH and CO<sub>2</sub> that are around 5%.<sup>6</sup> It is known that as the ceria particle size decreases in the nanometre length scale, there is an increasing density of defects in ceria mainly consisting in framework oxygen vacancies and ceria atoms in +3 oxidation state.<sup>15</sup> Apparently the presence of these defects is positive for the catalytic activity of CeO<sub>2</sub> for the carboxylation process (see later for the proposed reaction mechanism). IR spectroscopy has shown that upon admitting CO<sub>2</sub> into dehydrated np-CeO<sub>2</sub> or CeO<sub>2</sub> instantaneous appearance of strong bands attributable to metal carbonates is observed.6,8

We have found that the main reason of the moderate selectivity to 1,3-oxazolidin-2-one is its instability under the reaction conditions, undergoing decomposition probably by further reaction with diethanolamine giving unidentified oligomeric materials. To provide a better comparison between the activity of the two ceria samples (np-CeO<sub>2</sub> and CeO<sub>2</sub> (40 nm)) and considering the occurrence of consecutive reactions, it is convenient to compare time conversion plots rather than



Scheme 1 Reaction of  $\omega$ -aminoalcohols with CO<sub>2</sub> with the formation of cyclic carbamates.

Instituto de Tecnología Química, CSIC-UPV, Universidad Politécnica de Valencia, Av de los Naranjos s/n, 46022, Valencia, Spain. Fax: (+34)963877809

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Scheme 2 Reaction of diethanolamine with  $CO_2$  with formation of *N*-2-hydroxyethyl substituted oxazolidinone.

**Table 1** Catalytic activity for the reaction of diethanolamine with CO<sub>2</sub>. *Reaction conditions*: diethanolamine = 2 mmol, ethanol = 35 mmol, CO<sub>2</sub> = 7 bar, metal oxide = 75 mg, reaction time = 8 h, reaction temperature =  $160 \, ^{\circ}C^{a}$ 

Catalyst	Conv. <sup>b</sup> (%)	Sel. <sup>c</sup> (%)
np-CeO <sub>2</sub> (5 nm)	66	36
$\hat{CeO}_2$ (not-np)	36	82
Au $(0.01 \text{ wt})/\text{np-CeO}_2 (5 \text{ nm})$	48	46

<sup>*a*</sup> Other solid catalysts tested under the same conditions were γ-Al<sub>2</sub>O<sub>3</sub>, P-25 TiO<sub>2</sub>, ZrO<sub>2</sub>, MgO and Y<sub>2</sub>O<sub>3</sub> as well as Au/np-CeO<sub>2</sub> (5 nm) at gold loadings from 0.79 to 2.46 wt%. In all these cases no product formation was observed. <sup>*b*</sup> Conversion (%) = (initial mol diethanolamine – mol diethanolamine at 8 h) × 100/initial mol diethanolamine. <sup>*c*</sup> Selectivity (%) = (mol product formed/mol of converted diethanolamine) × 100.

single selectivity data at different conversion. Fig. 1 shows to the evolution of the reaction of diethanolamine with  $CO_2$  in the absence and in the presence of np-CeO<sub>2</sub> and CeO<sub>2</sub> (not np). As can be seen in this figure, ceria is required in order for diethanolamine to react with  $CO_2$ . The activity of np-CeO<sub>2</sub> is higher than that of the commercial not-np CeO<sub>2</sub>. However, as commented earlier, the resulting *N*-(2-hydroxyethyl) oxazolidinone is not stable under the reaction conditions, with decreased selectivity as the conversion increases.

As commented earlier, previous reports stated that Au nanoparticles increase the inherent activity of ceria for the transalkylation of organic carbonates with linear alcohols or for the carbamoylation of aromatic amines with dimethyl carbonate.<sup>8,16</sup> In the present case, however, it was found that Au nanoparticles, even at the smallest loading (0.01 wt%), significantly decreases np-CeO<sub>2</sub> activity that is suppressed at higher loadings (Table 1). We propose that this negative influence of Au arises from the fact that Au nanoparticles are covering the ceria defects (see mechanistic proposal below). Thus, the results presented in Table 1 constitute an example of a negative interaction of ceria with Au nanoparticles.



**Fig. 1** Conversion ( $\blacktriangle$ ,  $\blacklozenge$  and  $\blacksquare$ ) and selectivity ( $\triangle$  and  $\diamond$ ) for the reaction of diethanolamine with CO<sub>2</sub> in the presence of np-CeO<sub>2</sub> (5 nm) ( $\bigstar$  and  $\triangle$ ), commercial CeO<sub>2</sub> (40 nm) ( $\blacklozenge$  and  $\diamond$ ) and CeO<sub>2</sub> (non-np) ( $\blacksquare$ ). *Reaction conditions:* Diethanolamine = 2 mmol, ethanol = 35 mmol, CO<sub>2</sub> = 7 bar, metal oxide = 75 mg, reaction temperature = 160 °C.

**Table 2** Conversion and selectivity for the reaction of *N*-alkyl ethanolamines with CO<sub>2</sub>. *Reaction conditions*: *N*-alkyl ethanolamine = 2 mmol, ethanol = 35 mmol, CO<sub>2</sub> = 7 bar, catalyst = 75 mg, reaction time = 8 h, reaction temperature =  $160 \text{ }^{\circ}\text{C}$ 

$ \begin{array}{c} R' \\ R \end{array} \xrightarrow{\text{OH}} OH \xrightarrow{\text{CO}_2} O \\ EtOH \end{array} \xrightarrow{\text{O}} N-R' \\ R \end{array} $					
Catalyst	R	R′	Conv. (%)	Sel. (%)	
np-CeO <sub>2</sub> (5 nm)	Н	Me	68	88	
$CeO_2$ (40 nm)	Н	Me	48	90	
ZrO <sub>2</sub>	Н	Me	19	87	
$Al_2O_3$	Н	Me	12	60	
$np-CeO_2$ (5 nm)	Н	Et	80	85	
$np-CeO_2$ (5 nm)	Н	<i>n</i> -Pr	77	83	
$\hat{CeO}_2$ (40 nm)	Н	<i>n</i> -Pr	45	89	
$np-CeO_2$ (5 nm)	Me	Н	32	56	

After having found that nanoparticulated ceria promotes the reaction of  $CO_2$  with diethanolamine we have expanded the scope of the catalytic  $CO_2$  fixation by performing analogous reactions with ethanolamine derivatives. The results are presented in Table 2. As it can be seen, high conversions of the *N*-alkyl ethanolamines with good selectivity to *N*-alkyl 1,3-oxazolidin-2-one were obtained in all three cases, showing that the process is general.

Considering that *N*-methyl aminoethanol was the compound giving higher yields of the corresponding oxazolidinone, we re-screened the activity of the other metal oxides ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, P-25 TiO<sub>2</sub>, ZrO<sub>2</sub>, MgO and Y<sub>2</sub>O<sub>3</sub>). While *N*-methyl aminoethanol conversion in the presence of TiO<sub>2</sub>, MgO and Y<sub>2</sub>O<sub>3</sub> was below 6% after 8 h, Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> render the pentacyclic carbamate with moderate yield (Table 2). These data with *N*-methyl aminoethanol reconfirms the superiority of np-CeO<sub>2</sub> over the other oxides.

To test the heterogeneous nature of the catalysis, the reaction of *N*-methyl aminoethanol using np-CeO<sub>2</sub> as catalyst was initiated under the typical reaction conditions and the solid filtered from the hot solution after 90 min when the conversion was already 38%. The resulting clear solution after filtration was heated under the reaction conditions observing a further 11% *N*-methyl aminoethanol conversion. This indicates that leached Ce is responsible of about 22% of the conversion. Furthermore, chemical analysis of the filtered solution shows the presence of Ce corresponding to 0.2% of the initial Ce in the solid catalyst. Thus, the hot filtration test and chemical analysis shows that under the reaction conditions some Ce is dissolved and promotes the reaction in the liquid phase.

Nevertheless, the np-CeO<sub>2</sub> solid recovered after the reaction of *N*-methyl aminoethanol with CO<sub>2</sub> at 160 °C was reused three times without noting any significant activity decay or selectivity change towards *N*-methyl-1,3-oxazolidin-2-one. This is not surprising considering the small percentage of leached Ce. Apparently, although a minute fraction of np-CeO<sub>2</sub> becomes dissolved and acts in the homogeneous phase, np-CeO<sub>2</sub> can be almost completely recovered without losing activity for the CO<sub>2</sub> fixation by  $\omega$ -aminoalcohols.

In Table 2, the results of the reaction of 2-amino-1-propanol with  $CO_2$  are also included. It is interesting to note that

**Table 3** Conversion and selectivity for the reaction of  $\omega$ -aminoalcohols with CO<sub>2</sub> in the presence of np-CeO<sub>2</sub> as catalyst. *Reaction conditions*:  $\omega$ -aminoalcohol = 2 mmol, ethanol = 35 mmol, CO<sub>2</sub> = 7 bar, np-CeO<sub>2</sub> = 75 mg, reaction temperature = 160 °C, reaction time 6h.

Substrate	Conv. (%)	Sel. (%)	
2-Aminoethanol	58	87	
3-Aminopropanol	30	79	
4-Aminobutanol	20	76	

2-amino-1-propanol is widely available by dehydration and amination of glycerol.<sup>17</sup> Glycerol is a by-product of biodiesel and a surplus of glycerol is expected. Thus, there is a large incentive in developing products derived from glycerol such as 4-methyloxazolidin-2-one that is an nitrogenated analog of glycerol carbonate.

Finally, the influence of the ring size of the resulting cyclic carbamate was studied by using as starting materials the parent 2-aminoethanol, 3-aminopropanol and 4-aminobutanol to give 1,3-oxazolidin-2-one, 1,3-oxazinan-2-one and 1,3-oxazepinan-2-one, respectively. Table 3 show the data corresponding to the highest product yield. Further increase in  $\omega$ -aminoalcohol conversion leads to a decrease in the selectivity toward the cyclic carbamate.

Table 3 shows that as the size of the resulting ring increases, the corresponding heterocycle becomes disfavoured. It is interesting to note that for 2-aminoethanol and 3-aminopropanol, formation of a secondary product corresponding to a dimeric condensation was observed. Detection of this by-product supports our previous claims about decomposition of the cyclic carbamate under the reaction conditions (Scheme 3). Apparently in the case of secondary ethanolamines shown in Table 2, self-decomposition is disfavoured with respect to primary amines for steric reasons and the corresponding oxazolidinones are more stable. In any case, the data of Table 3 are again remarkable in the context of related  $CO_2$  fixation reactions with yields between 50 and 15%.

The reaction mechanism leading to the formation of cyclic carbamates and the differences among the ceria samples were studied by IR spectroscopy (see ESI<sup>†</sup>). It was observed that after CO<sub>2</sub> chemisorption and evacuation at 160 °C (the reaction temperature) using CH<sub>3</sub>OH as probe to characterize the active sites, np-CeO<sub>2</sub> is the only sample having acid sites able to form CH<sub>3</sub><sup>+</sup>, while commercial CeO<sub>2</sub> (40 nm) or Au/np-CeO<sub>2</sub> lack these sites. These acids sites are required to effect the esterification of carbamic acid into the cyclic carbamate.



Scheme 3 Proposed mechanism of cyclic carbamate decomposition and formation of dimeric diamines.

In conclusion, in the present work we describe that fixation of  $CO_2$  by bidentate  $\omega$ -aminoalcohols can be carried out using nanoparticulated ceria as catalyst. High conversions with good selectivity towards oxazolidinone were achieved for *N*-alkyl substituted aminoethanols. Our report is of interest in the context of Green Chemistry trying to develop new processes using  $CO_2$  as a C1 feedstock.

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## Notes and references

‡ *Materials*.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, P25 TiO<sub>2</sub>, MgO, CeO<sub>2</sub> (40 nm average size), non-nanoparticulated CeO<sub>2</sub> (non-np-CeO<sub>2</sub>) and amino alcohols were commercial samples (Aldrich). nanoparticulated CeO<sub>2</sub> (np-CeO<sub>2</sub>) and ZrO<sub>2</sub> were prepared by hydrolysis in aqueous solution of the corresponding soluble salts at controlled pH. as reported in the literature.<sup>8</sup> Au/CeO<sub>2</sub> was obtained from HAuCl<sub>4</sub> by a deposition–precipitation method as reported.<sup>16</sup>

*Reaction procedure.* Catalytic experiments were performed in reinforced glass reactors equipped with temperature and pressure controllers. For each reaction, the reactant mixtures were dissolved in ethanol (35 mmol) and placed into the reactor (2 mL capacity) together with the corresponding catalyst (75 mg). *n*-Decane was used as internal standard to determine conversions and selectivity. The reactors were sealed and deeply introduced into the silicone bath preheated at the required temperature. The reactions were conducted at autogeneous pressure. During the experiment, the magnetic stirring rate was fixed at 1000 rpm. Aliquots were taken from the reactor at different reaction times. Once the catalyst particles were removed from the solution by centrifuging at 12 000 rpm, the products were analyzed by GC-MS (Hewlett-Packard, 35 m capillary column of cross-linked 5% phenyl methylsilicone).

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