

Activity of ceria and ceria-supported gold nanoparticles for the carbamoylation of aliphatic amines by dimethyl carbonate*

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Abstract: Aliphatic amines react sluggishly with dimethyl carbonate (DMC) to give a mixture of N-methylation and carbamoylation. Nanoparticulated ceria as catalyst increases, in general, conversion and selectivity toward carbamoylation. This increase in catalytic activity and selectivity toward carbamoylation is even increased by deposition of Au nanoparticles on ceria. However, in contrast to aromatic amines for which a complete selectivity toward carbamoylation using ceria-supported Au nanoparticles can be achieved, the catalytic carbamoylation of aliphatic amines by ceria-supported Au nanoparticles occurs only with moderate selectivity.

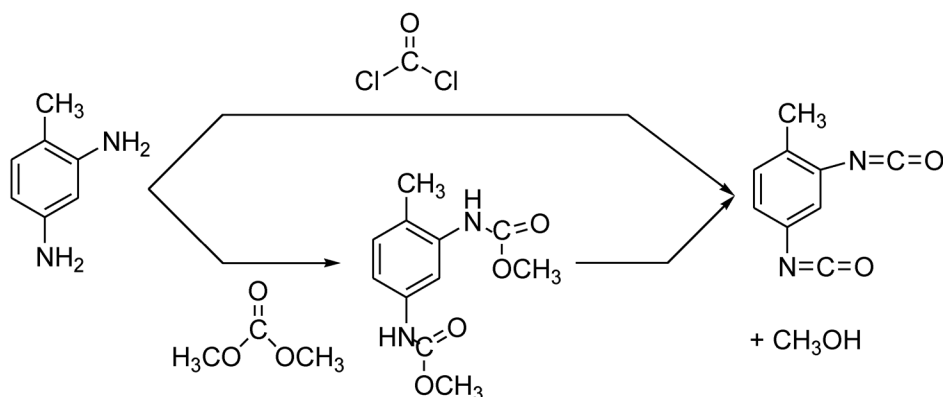
Keywords: carbamoylation; catalysts; gold; gold nanoparticles; green chemistry; phosgene-free synthesis of isocyanates.

INTRODUCTION

Carbamates are useful synthetic intermediates for the preparation of isocyanates, pesticides, and other compounds with biological activity [1]. Recently, we have reported that ceria-supported gold nanoparticles (Au/CeO₂) are highly selective and reusable heterogeneous catalysts for the preparation of *N*-aryl *O*-methyl carbamates by reacting aromatic amines with dimethyl carbonate (DMC) [2]. The corresponding aromatic carbamates can be transformed thermally or catalytically into the corresponding aromatic isocyanates. Aromatic diisocyanates derived from 2,4-diaminotoluene or bis-(aminophenyl)methanes are monomers of commercial polyurethanes [3]. The route based on the catalytic carbamoylation of aromatic diamines constitutes an alternative to the current industrial synthesis of aromatic diisocyanates based on the use of phosgene [4]. Phosgene is a deadly chemical that should be urgently replaced by other chlorine-free reagents, and the present reactions based on the use of phosgene should be replaced by other environmentally benign processes. One additional advantage of employing DMC as reagent instead of phosgene is that DMC can be eventually obtained from CO₂, which would make the synthesis of isocyanates based on renewable feedstocks rather than fossil fuels. Scheme 1 compares the two alternative routes for the production of toluene diisocyanate (TDI), the most important polyurethane co-monomer, based on phosgene or DMC.

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Scheme 1 Alternative synthetic routes for the preparation of TDI based on the use of phosgene or DMC.

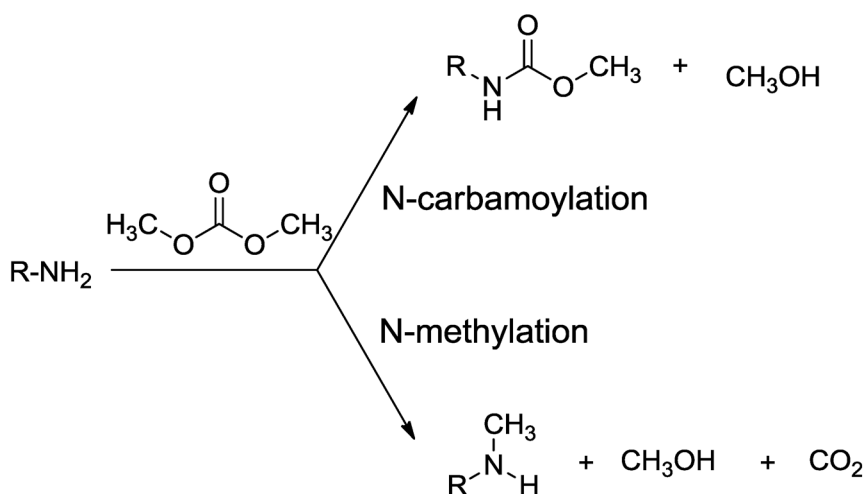
In the case of aromatic amines, it has been found that nanoparticulated CeO_2 , in contrast to other metal oxides, exhibits some intrinsic activity and selectivity for amine carbamoylation even in the absence of Au. However, the catalytic data showed that the inherent activity of CeO_2 is enhanced by the presence of Au nanoparticles at low loadings (<2 wt %) [2]. Considering the remarkable high catalytic activity of Au/ CeO_2 , it is of interest to expand its scope, exploring the performance of CeO_2 and Au/ CeO_2 for the reaction of DMC with aliphatic amines.

Aliphatic amines are significantly more nucleophilic than aromatic amines and, for this reason, they do react with DMC in the absence of any catalyst under conditions in which aromatic amines are unreactive. This thermal reaction between aliphatic amines and DMC can be unselective toward carbamoylation, and, therefore, this spontaneous, uncatalyzed process will compete and overlap with the catalyzed reaction and could make the overall product distribution unsuitable for industrial application.

Since the reported catalytic activity of Au/ CeO_2 for aromatic amines does not allow extrapolating the results for aliphatic amines owing to their distinctive reactivity, it is of much interest to determine the behavior of CeO_2 and Au/ CeO_2 for aliphatic amines. In the present work, we have undertaken a study showing that formation of *O*-methyl carbamates of aliphatic amines is also promoted by CeO_2 and Au/ CeO_2 with some exceptions, but that other unwanted products are also formed and the issue of a suitable heterogeneous catalyst and reaction conditions for the selective carbamoylation of aliphatic amines still remains unsatisfactorily solved.

DMC as reagent exhibits a dual behavior as methylating and carbamoylating reagent for amines (Scheme 2) [5]. In the present case, the target is to develop suitable heterogeneous catalysts for the selective carbamoylation of amines minimizing the formation of *N*-methylamines. In addition, the higher nucleophilicity of aliphatic amines may make unstable the primary carbamates that can undergo secondary reactions leading to the formation of some derivatives such as the corresponding isocyanates and ureas.

There are precedents in the literature reporting the ability of $\text{Sc}(\text{OTf})_3$ to act as homogeneous catalyst for the carbamoylation of aliphatic amines [6]. The proposed mechanism implies the coordination of the carbonyl group of DMC with Sc^{+3} acting as Lewis acid sites. Besides homogeneous catalysts, the carbamoylation of aliphatic amines has also been performed using the supernucleophilic amine 1,5,7-triazabicyclo[4.4.0]dec-5-ene covalently anchored on mesoporous MCM-41 silica [7]. However, the drawbacks of this modified MCM-41 are (i) the multistep preparation process needed to attach the organic base to the support, (ii) the limited stability of organocatalysts toward regeneration, and (iii) the incomplete selectivity toward carbamoylation of aliphatic amines. Development of alternative fully inorganic stable catalysts is still desirable, provided that it is selective toward carbamoylation.



Scheme 2 Dual reactivity of DMC as methylating and carbamoylating reagent.

Herein we report that, in general, CeO_2 promotes carbamoylation of benzyl and alkyl amines and that this catalytic activity is also increased by the presence of a low loading of Au nanoparticles. However, in contrast with aromatic amines, the selectivity toward carbamoylation under the conditions tested is never complete and even in some cases similar to the spontaneous, uncatalyzed process. The presence of unwanted products derived from N-methylation or secondary decomposition of carbamate is always observed, making the process still unsatisfactory.

RESULTS AND DISCUSSION

For the present study we have selected eight substrates including primary benzylic and alkyl amines and a secondary amine. Blank reactions in the absence of any solid catalyst have shown that aliphatic amines react slowly with an excess of DMC (amine/DMC molar ratio 1/15) at 120 °C to give a mixture of products. Under these conditions DMC acts as reagent and solvent. If these control reactions in the absence of any catalyst are allowed to react for a sufficiently long time, then the desired *N*-alkyl carbamate **2** is obtained, albeit with low to moderate selectivity and long reaction times. Table 1 indicates the products observed and lists their distribution for each of the substrates tested. This reactivity of aliphatic amines is in contrast to the behavior of aromatic amines that in the absence of catalyst do not react spontaneously with DMC even at higher temperatures. The blank controls indicate that the reactivity of benzyl amines is strongly influenced by the substituent present on the aromatic ring and that alkyl amines are highly reactive, giving moderate conversions in the absence of catalyst.

The product distribution of the uncatalyzed reaction depends on the structure and substitution of the amine, and it is difficult to be rationalized with the limited available data. However, it was observed that undesirable N-methylation was always taking place to a significant extent and that, frequently, it is the prevailing process. The occurrence of a spontaneous reaction of aliphatic amines with DMC under the reaction conditions should be detrimental for the overall selectivity since this process will take place concomitantly with the catalytic reaction.

Table 1 Conversion and selectivity for the reaction of benzyl and alkyl amines with DMC in the absence or presence of the catalysts. Reaction conditions: substrate/DMC molar ratio 1/15, reaction temperature 120 °C, time 5 h.

Amine	R ¹	R ²	Conversion of 1 (%)	Selectivity (%)			
				2	3	4	5
No catalyst							
a	Ph-	H-	12	10	2	16	72
b	p-CH ₃ -C ₆ H ₄ -	H-	43	53	5	19	23
c	Ph-	CH ₃ -	16	28	16	8	48
d	p-Cl-C ₆ H ₄ -	H-	16	35	6	19	40
e	C ₆ H ₁₂ -	H-	60	74	1	3	22
f	C ₈ H ₁₆ -	H-	45	39			61
g	C ₁₀ H ₂₀ -	H-	45	46			54
h	C ₆ H ₁₀ -	H-	22	10	15	20	55
CeO₂							
a	Ph-	H-	17	28	6	10	56
b	p-CH ₃ -C ₆ H ₄ -	H-	60	61	5	12	22
c	Ph-	CH ₃ -	27	10	1	11	78
d	p-Cl-C ₆ H ₄ -	H-	24	45	1	32	22
e	C ₆ H ₁₂ -	H-	73	72	10	3	15
f	C ₈ H ₁₆ -	H-	61	71			29
g	C ₁₀ H ₂₀ -	H-	57	95			5
h	C ₆ H ₁₀ -	H-	45	18	22	6	53
Au/CeO₂^a							
a	Ph-	H-	91	52	30	3	15
b	p-CH ₃ -C ₆ H ₄ -	H-	86	83	9	2	6
c	Ph-	CH ₃ -	74	62	35	3	
d	p-Cl-C ₆ H ₄ -	H-	81	54	2	1	3
e	C ₆ H ₁₂ -	H-	97	71	9	15	5
f	C ₈ H ₁₆ -	H-	52	69			31
g	C ₁₀ H ₂₀ -	H-	83	85			15
h	C ₆ H ₁₀ -	H-	38	19	23	11	47
Au/CeO₂^b							
a	Ph-	H-	96	86	12	1	1
b	p-CH ₃ -C ₆ H ₄ -	H-	92	95	3	1	1
c	Ph-	CH ₃ -	96	70	28	1	1
d	p-Cl-C ₆ H ₄ -	H-	90	89	1	1	9
e	C ₆ H ₁₂ -	H-	100	87	10	2	1
f	C ₈ H ₁₆ -	H-	58	80			20
g	C ₁₀ H ₂₀ -	H-	61	92			8
h	C ₆ H ₁₀ -	H-	38	26	31	8	35

^a10 wt % catalyst respect to amine.

^b10 wt % Au/CeO₂ (0.4 wt Au %) respect to amine.

^c20 wt % Au/CeO₂ (0.4 wt Au %) respect to amine.

When nanoparticulate CeO₂ (10 wt % with respect to the amine) was added as catalyst, somewhat higher conversions of the aliphatic amines were attained at the same reaction times. The results obtained

at 5 h reaction time using CeO_2 as catalysts are also summarized in Table 1. However, although in general the selectivity *O*-methyl carbamate **2** was somewhat improved (except in the case of 1-phenylethanamine, see Table 1) with respect to the uncatalyzed reactions, these values were still far from being satisfactory. Thus, formation of large amounts of *N*-methyl amines were still observed in agreement with the dual reactivity of DMC commented earlier. In addition, formation of significant percentages of the corresponding isocyanates **3** and even dialkyl ureas **4** arising from the secondary reaction of carbamates **2** was also observed. From the results obtained in the presence of ceria it can be concluded that in contrast to the behavior reported for aromatic amines where ceria exhibits high selectivity toward carbamoylation [4], in the case of aliphatic amines, the presence of ceria exerts only a moderate influence on the outcome of the reaction, improving slightly the selectivity toward carbamoylation, but without impeding the formation of *N*-methyl amines.

Activity of Au/ CeO_2

Considering the unsatisfactory catalytic performance of CeO_2 , it was interesting to determine whether or not the presence of Au nanoparticles at low loadings can improve the activity of CeO_2 as it has been observed for other reactions [8,9]. Starting from CeO_2 , Au nanoparticles were supported following standard deposition-precipitation method (see Experimental section) [10]. Au/ CeO_2 has been found to be a highly active catalyst for a wide reaction range including low-temperature CO oxidation [11], aerobic alcohol [11,12], and amine oxidation [13] and transalkylation of propylene carbonate [9] among other reactions [14]. The Au loading in Au/ CeO_2 , as determined by chemical analysis, was 0.4 wt %, which is a common value for this type of catalyst.

Transmission electronic microscopy (TEM) shows that the solid contains homogeneously distributed Au nanoparticles with an average size of 1.5 nm, deposited on ceria support (Fig. 1).

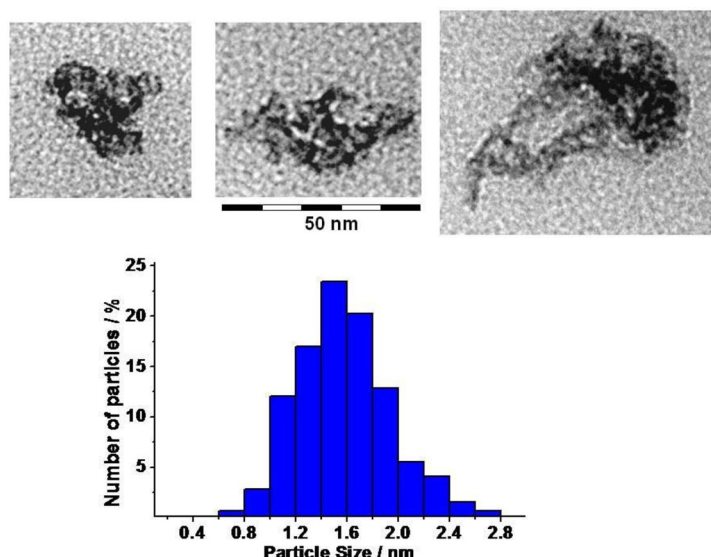


Fig. 1 Three representative TEM images of the Au/ CeO_2 (0.4 wt % of Au) sample used as catalyst in this work and statistical analysis of the particle size distribution.

Interestingly, the presence on CeO_2 of Au nanoparticles at the low loading prepared exhibits a dramatic effect increasing benzyl amine **1a** conversion and favoring notably the selectivity toward the

target *O*-methyl carbamate **2a**. In this way, in the presence of Au/CeO₂, **2a** was the major reaction product accompanied by significant amounts of the corresponding dibenzyl urea (**3a**) and still unsatisfactorily high percentages of *N*-methylbenzyl amine (**5a**).

Higher conversions of benzyl amine and selectivity to the target carbamate **2a** could be obtained by addition of larger amounts of Au/CeO₂, reaching a Au/amine **1a** molar ratio of 0.08. Table 1 summarizes the reaction data corresponding to the product distribution at 5 h reaction time using Au/CeO₂ as catalyst at two different Au/amine molar ratios.

To demonstrate the influence of the presence of Au and the superior catalytic activity of Au/CeO₂ over CeO₂ for benzyl amine (**1a**), Fig. 2 shows the time conversion plot for the reaction of this primary amine with DMC. For the sake of comparison, the plot contains the temporal evolution of the blank reaction in the absence of any catalyst as well as the plot of **1a** conversion of two batches using two different amounts of Au/CeO₂. As can be seen in Fig. 2, the conversion of benzyl amine in the absence of catalyst is relatively minor after 5 h reaction time. Nanoparticulated CeO₂ increases somewhat the benzyl amine conversion with respect to the blank, but the presence of Au nanoparticles at any of the two molar ratios improves substantially the catalytic performance of the ceria.

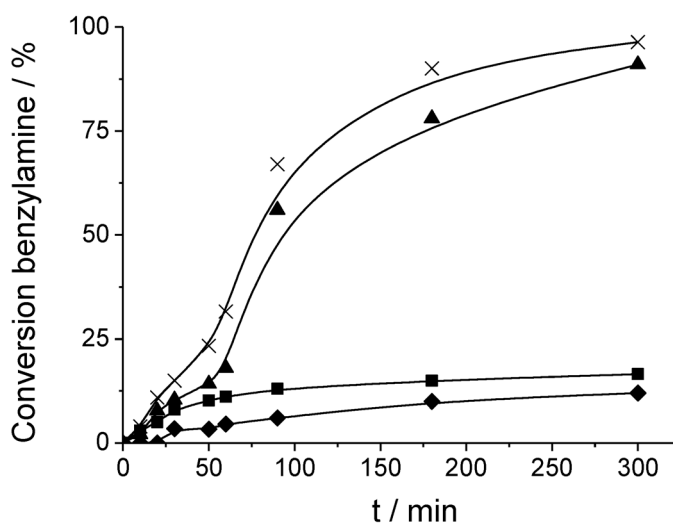


Fig. 2 Time conversion plot for the reaction of benzyl amine with DMC in the absence and in the presence of solid catalysts: blank (◆), CeO₂ 10 wt % (■), Au/CeO₂ 10 wt % (▲) and 20 wt % (×). Reaction conditions: substrate/DMC molar ratio 1/15, reaction temperature 120 °C.

If one considers the temporal profiles of formation of *N*-methylbenzyl amine (**5a**) and *N*-alkyl *O*-methyl carbamate **2a**, it appears that both compounds are primary products arising from parallel reactions of benzyl amine (**1a**) with DMC as indicated in Scheme 2. However, product **2a** is unstable under the reaction conditions, indicating that compound **2a** undergoes consecutive transformation, forming the secondary isocyanate **4a** and urea **3a** products. The superior catalytic activity of Au/CeO₂, particularly using a Au/amine ratio of 0.08 %, was confirmed for the other three benzyl amines **1b**, **c**, and **d** tested (see Table 1).

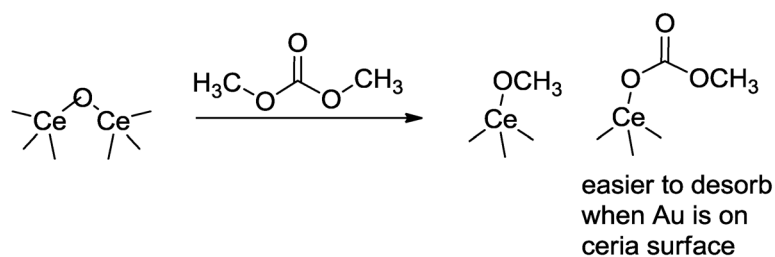
Considering the activity of CeO₂ and Au/CeO₂, it is worth commenting that the reaction of benzylamine (**1a**) with DMC in the presence of Au nanoparticles supported on TiO₂ (P-25) or Fe₂O₃ under analogous conditions only leads to the formation of *N*-methylbenzylamine (**5a**) with complete selectivity at 11 and 17 % of conversion **1a** for Au/ TiO₂ and Au/ Fe₂O₃, respectively.

The higher reactivity of alkyl amines **1e–h** compared to benzyl amines **1a–d** is reflected by the fact that the blank control already shows significant conversions of these alkyl amines in the absence of catalyst after 5 h (see Table 1). Probably due to this higher reactivity of alkyl amines, the influence of the presence of Au on ceria is much less remarkable in the case of alkyl amines **1e–h** as compared to benzyl amines. On the one hand, conversions of alkyl amines were not much increased by the presence of Au, whose deposition can even play an adverse role with respect to the activity of CeO₂, decreasing the conversion in a small percentage in the cases of octanamine (**1f**) and cyclohexanamine (**1h**). With respect to the selectivity for carbamoylation, the presence of Au plays a favorable role with respect to the blank uncatalyzed reactions except for hexanamine **1e**. However, with respect to the selectivity for carbamoylation of alkyl amines observed for CeO₂, deposition of Au seems to play a marginal role, and both solids CeO₂ and Au/CeO₂ exhibit similar selectivity values toward carbamate **2**. It should be noted that comparison of the catalytic performance is complicated by the fact that higher conversions are achieved when using Au/CeO₂ as catalyst. Importantly, in spite of the higher conversions reached in the presence of Au/CeO₂ for all the amines tested, the undesirable N-methylation was reduced considerably with respect to the uncatalyzed reaction. In contrast, CeO₂ in the absence of Au can form higher (in the case of **1e**) or similar (**1b** and **h**) percentages of N-methylation that the reaction carried out in the absence of any catalyst.

In general, the temporal profiles of the reactions with DMC of substituted benzyl amines and aliphatic amines in the absence and presence of catalysts follow a similar trend to that shown in Fig. 2 for the parent benzyl amine (**1a**). In the case of benzyl methyl amine (**1c**) and 4-chlorobenzyl amine (**1d**), the corresponding time conversion plots reveal that the reactions in the absence of catalyst exhibit an induction period for the formation of products. This induction period becomes shorter in the presence of catalysts and eventually disappears when a higher amount of Au/CeO₂ is present. Observation of this induction period suggests that any of the products such as the carbamate or the urea can act as organocatalyst of the reaction. The strong hydrogen bonds of carbamates [15] and ureas [16] are known to be responsible for some catalytic activity of this type of compounds for some substitution reactions.

The most important feature from the data in Table 1 is (in general, with two exceptions) for reactive alkyl amines **1f** and **g** deposition of Au nanoparticles decreases N-methylation of amines for DMC, boosting the catalytic activity of CeO₂. As commented earlier, there are opposite precedents in the literature showing that the presence of Au can increase or decrease the catalytic activity inherent to CeO₂. Thus, the carbamoylation of aromatic amines and transalkylation of organic carbonates is accelerated by the presence of Au in small percentages on nanoparticulated CeO₂ [2,9], while for the reaction of CO₂ with ω-amino alcohols, the presence of Au is detrimental for the catalytic activity of nanoparticulated ceria [17]. The present results will constitute an additional example of how low loadings of Au below 1 wt % influence the intrinsic low activity of nanoparticulated ceria.

In order to understand the influence of Au, IR spectroscopic characterization of DMC on CeO₂ was carried out. Upon adsorption of DMC on CeO₂, the presence of new bands at 1104 and 1588 cm⁻¹ attributable to organic carbonates and methoxy groups, respectively, was observed. This indicates that on the surface of CeO₂, DMC splits, forming a methoxy group and a methoxycarbonyl as indicated in Scheme 3. In order to assess the reactivity of the two fragments, methoxycarbonyl and methyl, a thermal treatment was performed by evacuating the solid after DMC absorption at 150 °C under vacuum. It was observed that under these conditions the band corresponding to methoxycarbonyl undergoes a significant decrease compared to that corresponding to the methoxy group. This easier desorption of surface-bound methoxycarbonyl groups would be indicative of their higher reactivity. Analogous thermal treatment for Au/CeO₂ reveals that the presence of Au nanoparticles on CeO₂ decreases significantly the temperature required to desorb the methoxycarbonyl groups that start desorbing under vacuum even at 100 °C. We interpret these spectroscopic observations as indicating that the presence of Au nanoparticles favors the transfer of methoxycarbonyl moiety to the amine as it has previously been observed also for aromatic amines [2]. However, other alternative interpretations besides the promo-



Scheme 3 Mechanistic proposal to rationalize the catalytic activity of CeO₂ as support favoring carbamoylation.

tional effect of Au on the activity of ceria such as that Au deposition masks basic sites of ceria, modifying their activity cannot be excluded at this moment.

The heterogeneity of the catalytic process and the absence of leaching using Au/CeO₂ (0.4 wt %) were studied by performing the *hot filtration* test and chemical analysis of the liquid phase and the solid after the reaction. Thus, when the reaction of 4-chlorobenzyl amine (**1d**) was performed under the reaction conditions indicated in Table 1 and the solid was filtered after 30 min (22 % conversion), it was observed that the resulting liquid undergoes a minor increase in conversion (33 %) after 5 h. Comparison of this result with that observed in the presence of solid catalyst clearly establishes that most of the catalytic activity in the presence of Au/CeO₂ has to be attributed to the presence of the solid catalyst. In addition, chemical analysis showed that the concentration of Au in the organic phase after the reaction is below the detection limit (0.5 ppm) while that of Ce is 0.16 ppm. In addition, chemical analysis of the used Au/CeO₂ coincides with that of the fresh sample.

Reusability of Au/CeO₂ and catalyst productivity was also tested for 4-chlorobenzyl amine (**1d**). It was found that filtration of the Au/CeO₂ catalyst followed by washings with basic water (pH 10 with NaOH 0.2 M) and drying renders a sample with the same catalytic performance as the fresh material. In an additional experiment under the conditions of Table 1, but using 1 wt % of Au/CeO₂, the reaction was allowed to occur till completion. It was observed that also in this experiment using 10 times more substrate than the usual conditions of Table 1, complete conversion with similar product distribution was attained, although at a longer time.

CONCLUSIONS

In contrast to aromatic amines, aliphatic amines react with DMC in the absence of catalyst to give a mixture of carbamoylation and methylation products. Primary alkyl amines are particularly reactive toward DMC compared to benzyl amines. In the present work, we have shown that CeO₂ increases conversion, particularly for less reactive benzyl amines, and improves the selectivity toward carbamoylation. Deposition of Au nanoparticles on CeO₂ increases even further the conversions of the aliphatic amines, reducing the selectivity toward undesirable N-methylation. These results of benzyl and alkyl amines sharply contrast with the catalytic data obtained for aromatic amines, where the selectivity toward *O*-methyl carbamate using Au/CeO₂ was complete. In addition, it was also found that the higher reactivity of aliphatic amines compared to aromatic amines is responsible for the secondary reaction of primary *O*-methyl carbamates with unreacted amines leading to isocyanates and ureas, two processes that are not observed for aromatic amines. In these reactions, the Au/CeO₂ catalyst can be reused without decrease of the catalytic activity, and no leaching of Au was detected.

EXPERIMENTAL

Preparation of CeO₂ nanoparticles

Nanoparticulated ceria was prepared, adding at ambient temperature under continuous magnetic stirring an ammonia aqueous solution (1.12 L, 0.8 M) over 375 mL of a Ce(NO₃)₄ (0.8 M). The colloidal dispersion of CeO₂ nanoparticles was heated in a polyethylene terephthalate vessel at 100 °C during 24 h. The resulting yellow precipitate was filtered and dried under vacuum overnight. The cerium oxide synthesized has, owing to the small size of the nanoparticles, a surface area of 180 m² g⁻¹

Preparation of Au/CeO₂

Au supported on nanoparticulated cerium oxide was prepared using a solution of 200 mg of HAuCl₄·3H₂O in 40 ml of deionized water that was brought to pH 10 by addition of a solution of NaOH 0.2 M. Once the pH value was stable, the solution was added to a slurry containing colloidal CeO₂ (10 g) in H₂O (50 ml). After adjusting the pH to 10 with NaOH 0.2 M, the slurry was left under vigorous stirring for 18 h at room temperature. The Au/CeO₂ solid was then filtered and exhaustively washed with distilled water until no traces of chlorides were detected by the AgNO₃ test. This is an important treatment since traces of Cl⁻ remain strongly bonded to Au and are highly detrimental for the overall activity. The catalyst was dried at room temperature under vacuum. The total Au content of the final catalyst was 0.4 % as determined by chemical analysis. Under this procedure, Au nanoparticles of 1.5 nm average size supported on CeO₂ are obtained.

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 DMC (35 mmol) and placed into a conical reactor (2 ml capacity) together with the corresponding catalyst (10 wt % of CeO₂ or 10 or 20 wt % of Au/CeO₂, with respect to amine). Benzyl and alkyl amines used in this study are commercially available from Sigma-Aldrich with purities higher than 95 %. The samples were used as received. *n*-Dodecane was used as internal standard to determine conversions and selectivity by gas chromatography (GC). 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 reaction mixtures were magnetically stirred at 1000 rpm with a stirring bar of the appropriate size. Aliquots (100 μl) were taken from the reactor at different reaction times through an outlet that fits into a syringe. Once the catalyst particles were removed from the solution by filtration, the products were analyzed by GC-MS (Hewlett-Packard, 35 m capillary column of cross-linked 5 % phenyl methyl-silicone). Only experiments with mass balances ≥95 % were considered.

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REFERENCES

1. (a) M. Aresta, A. Dibenedetto. *Dalton Trans.* 2975 (2007); (b) Y. Ono. *Appl. Catal., A* **155**, 133 (1997); (c) T. Sakakura, K. Kohno. *Chem. Commun.* 1312 (2009).
2. R. Juárez, P. Concepcion, A. Corma, V. Fornes, H. Garcia. *Angew. Chem., Int. Ed.* **49**, 1286 (2010).
3. K. Plotr. *Prog. Mater. Sci.* **52**, 915 (2007).
4. R. Juárez, A. Corma, H. Garcia. *Top. Catal.* **52**, 1688 (2009).
5. (a) P. Tundo. *Chim. Oggi* **22**, 31 (2004); (b) P. Tundo, M. Selva. *Acc. Chem. Res.* **35**, 706 (2002); (c) P. Tundo, M. Selva. *Met. Reag. Green Chem.* 77 (2007).
6. (a) M. Distaso, E. Quaranta. *Tetrahedron* **60**, 1531 (2004); (b) M. Distaso, E. Quaranta. *Appl. Catal., B* **66**, 72 (2006); (c) M. Distaso, E. Quaranta. *J. Catal.* **253**, 278 (2008).
7. (a) R. Ballini, D. Fiorini, R. Maggi, P. Righi, G. Sartori, R. Sartorio. *Green Chem.* **5**, 396 (2003); (b) S. Y. Huang, J. Ma, J. P. Li, N. Zhao, W. Wei, Y. H. Sun. *Catal. Commun.* **9**, 276 (2008); (c) R. Juárez, A. Padilla, A. Corma, H. Garcia. *Catal. Commun.* **10**, 472 (2009); (d) Y. V. S. Rao, D. E. De Vos, P. A. Jacobs. *Angew. Chem., Int. Ed.* **36**, 2661 (1997).
8. R. Juárez, P. Concepcion, A. Corma, V. Fornes, H. Garcia. *Angew. Chem., Int. Ed.* **49**, 1286 (2009).
9. R. Juárez, A. Corma, H. Garcia. *Green Chem.* **11**, 949 (2009).
10. (a) M. Haruta. *Catal. Today* **36**, 153 (1997); (b) M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M. J. Genet, B. Delmon. *J. Catal.* **144**, 175 (1993).
11. S. Carrettin, P. Concepcion, A. Corma, J. M. Lopez Nieto, V. F. Puentes. *Angew. Chem., Int. Ed.* **43**, 2538 (2004).
12. A. Abad, A. Corma, H. Garcia. *Chem.—Eur. J.* **14**, 212 (2008).
13. A. Grirrane, A. Corma, H. Garcia. *J. Catal.* **264**, 138 (2009).
14. A. Corma, H. Garcia. *Chem. Soc. Rev.* **37**, 2096 (2008).
15. P. Galzerano, D. Agostino, G. Bencivenni, L. Sambri, G. Bartoli, P. Melchiorre. *Chem.—Eur. J.* **16**, 6069 (2010).
16. (a) M. Shi, X. G. Liu. *Org. Lett.* **10**, 1043 (2008); (b) M. T. Robak, M. Trincado, J. A. Ellman. *J. Am. Chem. Soc.* **129**, 15110 (2007); (c) D. J. Maher, S. J. Connon. *Tetrahedron Lett.* **45**, 1301 (2004).
17. R. Juárez, P. Concepción, A. Corma, H. Garcia. *Chem. Commun.* **46**, 4181 (2010).