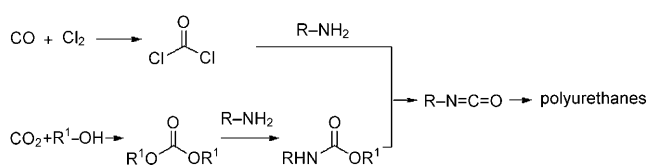


Gold-Catalyzed Phosgene-Free Synthesis of Polyurethane Precursors**

Raquel Juárez, Patricia Concepción, Avelino Corma,* Vicente Fornés, and Hermenegildo García*

Aromatic polyurethanes are manufactured by a chemical route which involves the use of phosgene as a reactant. An alternative catalytic green process that avoids phosgene by using dimethyl carbonate (DMC) instead, is presented herein. Typically DMC reacts with aromatic amines to yield N-methylation products, but with the catalyst developed herein selective N-carbamoylation takes place with a greater than 99 % selectivity at full conversion. The process involves a reusable solid catalyst derived from gold on nanocrystalline ceria. Besides aromatic amines, the catalyst also allows the reaction to proceed directly from nitroaromatics through a one-pot cascade reaction. This finding opens the possibility for an environmentally friendly route for the carbamoylation of aromatic amines that could be based on CO₂ as a primary feedstock.

The current industrial route for manufacturing polyurethanes and polycarbonates is based on the use of phosgene (Scheme 1).^[1,2] However, owing to the high toxicity of phosgene there is an urgent need to develop alternative reactants. Several phosgene-free syntheses of polyurethane



Scheme 1. Synthetic routes to polyurethanes involving either phosgene or organic carbonates.

precursors have been reported, but they either generate waste such as halide salts^[3] or CO₂,^[4,5] or they require more than a stoichiometric amount of a strong base;^[6] one of these methods employs a reusable heterogeneous catalyst. The reaction of aniline with *O*-methyl carbamate in methanol can be carried out with 6 % ZnCl₂ or Zn(AcO)₂, but these

catalysts remain in the reaction mixture and purification is needed to separate the resulting inorganic salts from the products.^[7] In addition, these catalysts cannot be reused in subsequent runs. In this regard the use of organic carbonates for the N-carbamoylation of aromatic amines could represent a “green” alternative to phosgene (Scheme 1), since the only by-product will be an alcohol, which can be recycled to form the dialkyl carbonate. If carbamates can be selectively formed by N-carbamoylation of aromatic amines, then they can be easily transformed into the corresponding polyurethanes (Scheme 1).^[8–10]

An overall process based on DMC will be highly favorable from an environmental point of view not only because of the phosgene replacement, but also because the carbonyl groups in the polyurethanes will be derived from CO₂ through DMC (Scheme 1).^[8–12] Although the current industrial production of DMC still uses oxidative carbonylation of methanol, novel routes based on the use of CO₂ as a feedstock are ready to be implemented.^[13,14] CO₂ can be obtained from air or, more favorably, it can be generated from combustion or fermentation processes. Therefore, fermentation can simultaneously provide the alcohol and the CO₂ needed for the synthesis of organic carbonates, making the whole route CO₂-neutral with doubtless advantages from the point of view of sustainability and environmental considerations.^[15] In contrast to the catalytic CO₂-neutral route presented herein, other alternatives based on CO, such as the reductive carbonylation of nitroarenes and oxidative carbonylation of amines, are based on the use of CO coming from nonrenewable fossil fuels and may generate two equivalents of CO₂ in the process. Therefore, processes based on carbonylation contribute to the increase of CO₂ in the environment, and considering the large production scale of aromatic polyurethanes and the Kyoto agreement regarding the reduction on CO₂, these processes are unfavorable compared to the one reported herein.

Notably, N-carbamoylation of aliphatic amines with DMC to form the corresponding carbamates is already well-known. However, the production of aromatic polyurethanes, which account for about 85 % of the market, still requires the use of phosgene. The reason for this is that the industrially relevant aromatic diamines react with DMC to preferentially afford the N-methylation product with some minor amount of the N-carbamoylation product.

Herein we show that gold nanoparticles supported on nanoparticulated ceria is an efficient and reusable solid catalyst for the selective N-carbamoylation of aromatic amines, and more specifically for the desired dicarbamoylation of 2,4-diaminotoluene (DAT), which is the most important aromatic amine for polyurethane production. Moreover,

[*] R. Juárez, Dr. P. Concepción, Prof. A. Corma, Prof. V. Fornés, Prof. H. García
Instituto Universitario de Tecnología Química UPV-CSIC
Universidad Politécnica de Valencia
Av. De los Naranjos s/n, 46022 Valencia (Spain)
Fax: (+34) 963-877-809
E-mail: acorma@itq.upv.es
hgarcia@qim.upv.es

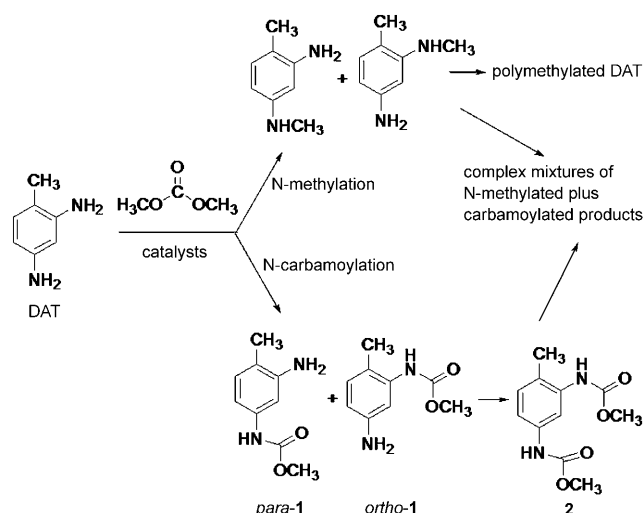
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we show that by using a single gold catalyst it is possible to combine the hydrogenation of nitroaromatics with the N-carbamoylation reaction in a one-pot catalytic process; this reaction requires only hydrogen and DMC as the reagents and produces methanol as the only by-product. Methanol can be reused for the DMC synthesis. When DAT is reacted with DMC, two reactions can in principle occur: The desired N,N'-dicarbamoylation and the formation of the undesired N-methyl derivatives. Since there are two amino groups in the DAT molecule, this can lead to a complex mixture of products as indicated in Scheme 2.

The reactions were carried out using an excess of DMC as the solvent. When the reaction of DAT with DMC was carried out in the presence of the conventional Lewis acid $\text{Zn}(\text{OAc})_2$,^[16] we found a high conversion of DAT with a modest yield for the desired dicarbamoylated product **2**, which resulted from the formation of significant amounts of mono-carbamoylated products *para*-**1** and *ortho*-**1**, and N-methylated products (Table 1, entry 1). Furthermore when the $\text{Zn}(\text{OAc})_2$ catalyst was recovered from the reaction media and reused, the yield for the N-carbamoylated products was even lower because of the decomposition of $\text{Zn}(\text{OAc})_2$ and the formation of inactive ZnO (entries 2 and 3). Organo-catalysts^[17] and transition-metal exchanged zeolites^[18] also promote N-methylation of DAT with either none or very minor amounts of N-carbamoylation occurring.

As a result of conventional solid Lewis acids not being able to promote the required N-carbamoylation, and considering the ability of gold, specifically supported gold, to interact and activate CO as well as other reactants,^[19,20–23] we considered the possibility of using gold to activate DMC. If such an activation of the CO moiety promoted the transfer of a methoxycarbonyl group rather than the transfer of the methyl group, the preferred process would be the formation of carbamates. We first studied the reaction of DAT with DMC over a catalyst derived from gold (0.44 wt %) supported on nanocrystalline CeO_2 (5 nm diameter). Transmission electron microscopy (TEM) showed that a large fraction of the gold particles in this catalyst were within 2–5 nm in diameter (see Figure S1 in the Supporting Information). The time/conversion plot for the reaction of DAT with DMC in the presence of Au/ CeO_2 (0.44 wt %) is given in Figure 1, and the results obtained after 7 hours of reaction time are compared with those obtained using other catalysts (Table 1). Interestingly, by using the Au/ CeO_2 catalyst the yield of the dicarbamoylated **2** was higher than 95% at a 99% conversion of DAT.



Scheme 2. Possible products derived from DAT as it undergoes N-methylation and N-carbamoylation reactions.

This result is remarkable, and becomes more relevant as the catalyst can be reused, at least three times, while maintaining a 99% conversion and a yield of up to 99% (entries 4 and 5). Importantly, when using the commercially available CeO_2 support, which has larger particles (40 nm) relative to the nanocrystalline CeO_2 , the catalyst activity and product yields were much lower (entry 6). Gold-free nanocrystalline CeO_2

Table 1: Results for the reaction of DAT with DMC in the presence of a series of catalysts.^[a]

Entry	Catalyst	Mass balance [%] ^[b]	DAT Conv. [%] ^[b]	<i>ortho</i> - 1 + <i>para</i> - 1 [%] ^[b]	Yield of 2 [%] ^[b]	N-Methylated product [%] ^[b]
1	$\text{Zn}(\text{OAc})_2$ Fresh	95 ± 3	99	36	25	39
2	$\text{Zn}(\text{OAc})_2$ After one use	95 ± 3	32	3	1	96
3	ZnO (40 nm)	97 ± 3	16	1	–	99
4	Au/ CeO_2 (0.44 %) Fresh	99 ± 2	99	4	96	–
5	Au/ CeO_2 (0.44 %) 3rd reuse	98 ± 2	99	–	100	–
6	Au/ CeO_2 (0.44 %; 40 nm)	99 ± 3	65	73	–	27
7	CeO_2 (5 nm)	97 ± 3	92	48	52	–
8	CeO_2 (40 nm)	97 ± 3	–	–	–	–
9	Au/ TiO_2 (0.44 %)	99 ± 3	58	10	–	90
10	Au/ Fe_2O_3 (0.44 %)	95 ± 3	27	–	–	100
11	Pd/ CeO_2 (0.44 %)	96 ± 3	87	34	65	1
12	Pd/ TiO_2 (1.5 %)	95 ± 3	10	4	–	96
13	Pt/ TiO_2 (1.5 %)	98 ± 2	8	–	–	100
14	Au(core)–Pd(shell)/ TiO_2	99 ± 2	40	77	3	20

[a] Reaction conditions: DAT (0.98 mmol, 120 mg), DMC (29.69 mmol, 2.67 g), catalyst: Au, Pd, Pt, Zn (0.5% mol respect to DAT), CeO_2 and ZnO (100 mg), 7 h, 140 °C. [b] Determined using GC/MS methods.

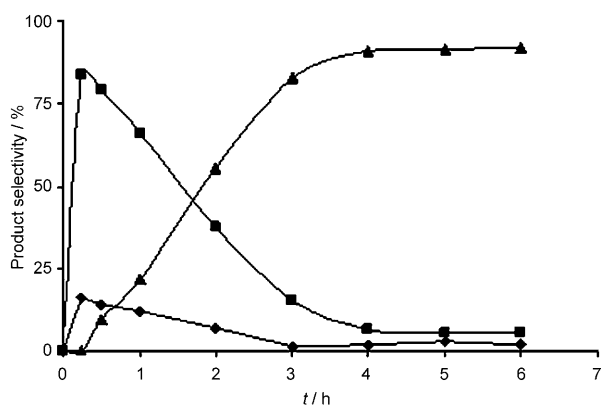


Figure 1. Product selectivity for the reaction of DAT and DMC in the presence of Au/CeO₂ (0.44 %; DAT/DMC mol ratio 30, $T = 423$ K). *ortho*-1 (◆), *para*-1 (■), 2 (▲).

also gives high selectivity for N-carbamoylation, but lower activities than Au/CeO₂ (entries 7 and 8).

At this point we were able to conclude that: a) in our hands, nanocrystalline CeO₂ is a selective carbamoylation catalyst; b) the presence of gold on the nanocrystalline catalyst strongly boosts activity to the desired dicarbamoylation product; and c) gold on nanocrystalline ceria is a reusable catalyst.

Since it has been shown^[13] that the nature of the support plays an important role in gold catalysis,^[24] we also used gold supported on TiO₂ and Fe₂O₃, and the resultant catalysts form the N-methylated products in high yield (entries 9 and 10). Meanwhile when gold was supported on carbon, an almost equal amount of N-methylation and monocarbamoylation occurred without formation of the desired product 2. Palladium supported on ceria gives much lower yields of the desired product 2 (entry 11), relative to that obtained using gold, but the yield of the undesired N-methylation product is still very low. In contrast, palladium or platinum supported on titania yields almost exclusively N-methylation products (entries 12 and 13). However, core(Au)-shell(Pd) nanoalloys supported on titania^[25] exhibit an intermediate product yield (entry 14). This indicates that both the support and the noble metal play a role in the catalysis and opens the possibility to develop other systems with even higher activity than our current Au/CeO₂ catalyst. Among the different supports studied here nanocrystalline CeO₂ gives, by far, the best catalytic performance.

The results obtained with DAT can be extended to other aromatic amines and organic carbonates. We have observed that Au/CeO₂ can selectively catalyze the N-carbamoylation of various *para*-substituted anilines with essentially complete conversions and yields to the N-carbamoylation product (see Table S1 in the Supporting Information). Au/CeO₂ also catalyzes the selective and complete N-dicarbamoylation of DAT using diethyl carbonate.

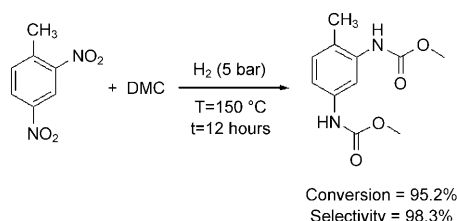
With the aim of gaining a better understanding of what occurs at the molecular level on the surfaces of CeO₂, Au/CeO₂, and Au/TiO₂, and to explain why the two latter catalysts behave so differently, we carried out an in situ FTIR spectroscopy study. The results given in Figure S2 in the

Supporting Information, show that DMC adsorbs dissociatively onto the CeO₂ surface, giving methoxy (IR bands at 1104 and 1044 cm⁻¹)^[26] and carbonate species (IR band at 1588 cm⁻¹).^[27] Desorption at increasing temperatures (see Figure S3 in the Supporting Information) indicate an easier desorption (potentially higher reactivity) of carbonate than the methoxy species, the latter remaining practically unchanged up to 393 K under vacuum. We have seen that these strongly adsorbed methoxy species are exactly the same as those formed when adsorbing pure methanol onto the nanocrystalline CeO₂.

When aniline (1606 cm⁻¹) was introduced into the IR cell after adsorbing DMC, and the wafer was heated at 303 K, the band corresponding to the carbonates slowly starts to disappear. At 393 K the band associated with the carbonate (1588 cm⁻¹) has mostly disappeared, whereas the methoxy groups have only partially disappeared; higher temperatures are required to achieve their full release (Figure S4a in the Supporting Information).

In the case of the Au/CeO₂ sample, the same bands and qualitative behavior as that of CeO₂ is observed, however, the most remarkable difference being that during the in situ reaction with aniline, the band belonging to the surface carbonates disappears faster at room temperature than with CeO₂ and has mostly disappeared at 343 K. (Figure S4b). Meanwhile on Au/CeO₂ the presence of a band at 1656 cm⁻¹, which can be attributed to the carbonyl group of the carbamate, is observed. On the contrary, for the nonselective Au/TiO₂, DMC also adsorbs dissociatively but the methoxy groups (1157, 1121, and 1054 cm⁻¹) are much easily desorbed than with Au/CeO₂ (see Figure S5 in the Supporting Information). Furthermore, the carbonate species (1566 cm⁻¹) are very strongly adsorbed. In this case, when aniline was introduced, the methoxy band starts to disappear already at room temperature and completely disappears at 343 K, whereas the bands at 3415, 1307, and 1287 cm⁻¹, associated with methylaniline, are formed.^[28] In contrast, a broader IR band at 1574 cm⁻¹, together with bands at 2956 and 2856 cm⁻¹ associated to the formation of some formate species, are also observed.^[29] Bands representing methylaniline and the formate species increase in intensity with increasing reaction temperature (see Figure S6 in the Supporting Information). The in situ results obtained with Au/CeO₂ and Au/TiO₂ nicely explain why N-methylation was preferentially observed with Au/TiO₂ whereas carbamoylation was the preferred reaction product during the previous batch reactor experiments.

Supported gold, particularly Au/TiO₂, is a selective catalyst for the hydrogenation of aromatics.^[30,31] Thus, a two-step process in which Au/TiO₂ effects the hydrogenation and subsequently Au/CeO₂ promotes the N-carbamoylation appears to be a general route to access aromatic carbamates. We have explored the possibility of combining these two reactions in a single-pot process to produce the dicarbamoylation of DAT, which is by far the most relevant aromatic N-carbamoylated product from the industrial point of view. The two-step, one-pot process requires the treatment of 2,4-dinitrotoluene with DMC under H₂ and using Au/CeO₂ as catalyst (Scheme 3). The results presented show that it is possible to achieve high conversion of 2,4-dinitrotoluene with



Scheme 3. One-pot reaction of 2,4-dinitrotoluene with DMC.

excellent yields of the product **2** by means of the one-pot procedure. The carbamoylation also occurs at 120 °C with a 99 % yield and 89 % conversion after a 14 hour reaction time.

In conclusion, an active, selective, and reusable catalyst based on Au/CeO₂ has been found for reacting aromatic amines with DMC to produce a dicarbamoylated product required for the synthesis of aromatic polyurethanes. This process opens a new route for polyurethane production that avoids the use of phosgene and CO while fixing CO₂ through the reactant DMC without generating any by-product except recyclable methanol or ethanol. Furthermore, through a one-pot process requiring only hydrogen, DMC, and a single catalyst, it is possible to convert 2,4-dinitrotoluene directly into its corresponding dicarbamate.

Experimental Section

Catalyst preparation: Zn(OAc)₂ and ZnO were commercial samples supplied by Sigma–Aldrich.

CeO₂ nanoparticles: Nanoparticulated ceria was prepared by adding an aqueous ammonia solution (1.12 L, 0.8 M) to 375 mL of a Ce(NO₃)₃ (0.8 M) at ambient temperature with continuous stirring. The colloidal dispersion of CeO₂ nanoparticles was heated in a polyethylene terephthalate vessel at 373 K for 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 very large surface area (180 m² g^{−1}).

Au/CeO₂: A solution of HAuCl₄·3H₂O (200 mg) in deionized water (40 mL) 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 vigorously stirred 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. These washes are important as traces of Cl[−] remain strongly bonded to gold 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 0.44 % as determined by chemical analysis. Under this procedure, 3–4 nm gold nanoparticles (average size) supported on CeO₂ were obtained. Another Au/CeO₂ sample containing a higher Au loading (1.60 wt %) was prepared following an analogous procedure but instead using 60 mg of HAuCl₄·3H₂O for 1.0 g of CeO₂.

The Au/TiO₂ catalyst consists of 1.5 wt % gold on TiO₂ and was supplied by the World Gold Council (reference catalysts, Type A). It can also be prepared by depositing the gold from an aqueous solution of HAuCl₄ (Alfa Aesar) onto a sample of TiO₂ (P25 Degussa). The deposition precipitation procedure is done at 343 K and pH 9, using NaOH (0.2 M) to maintain a constant pH over 2 h. Under these conditions, gold deposition occurs with 80 % efficiency. The catalyst is then recovered, filtered, washed with deionized water, and dried at 373 K overnight. Finally, the powder is calcined at 673 K in air for 4 h.

Following this procedure, 3.5 nm gold nanoparticles supported on TiO₂ are obtained.

Core-shell Au(core)–Pd(shell)–TiO₂ was prepared by stirring a solution of Au/CeO₂ (2 g; gold content 0.44 wt %) in water and an acetone dissolution of [PdCl₂(PhCN)₂] (150 mL, 2.5 × 10^{−4} M). The slurry was vigorously stirred at room temperature for 4 h. The solid was then filtrated, exhaustively washed with distilled water, and then dried at 373 K overnight. The solid was then reduced with 1-phenylethanol at 433 K for 2 h. The catalyst was then washed, filtered, and dried at room temperature for 12 h. The final Pd content was found to be 0.5 wt % by atomic absorption analysis.

Pd/TiO₂ and Pt/TiO₂ catalysts were prepared by impregnation of TiO₂ (2 g; Degussa P25, 10 g, S_{BET} = 55 m² g^{−1}) with a solution of PdCl₂ (0.345 g; Aldrich, 60 % purity) or H₂PtCl₆·6H₂O (0.28 g; Aldrich), respectively, in H₂O (7 mL; milliQ). The slurry was stirred for 2 h at room temperature, then all the liquid was evaporated and the solid was dried at 373 K overnight and then reduced with 1-phenylethanol at 433 K for 2 h. The catalyst was then washed, filtered, and dried at room temperature for 12 h. The final Pd or Pt content was found to be 5 wt % by atomic absorption analysis.

Reaction procedure: Experiments were performed in reinforced glass reactors equipped with temperature and pressure controllers. The reactions were carried out using an excess of DMC as the solvent. For each reaction, a mixture of DAT (1 mmol) and DMC (30 mmol) was placed into the reactor (3 mL capacity) together with an appropriate amount of catalyst. The DAT and DMC used in this study are commercially available from Sigma–Aldrich with purities higher than 95 %. *n*-Dodecane was used as an internal standard for the determination of the conversion and product yields. The reactors were sealed and H₂ was introduced (5 bar). The reactor was then placed in a preheated silicone bath at 140 °C. During the experiment, the stirring rate was fixed at 1000 rpm (magnetic stirring). Aliquots were taken from the reactor at different reaction times, and the catalyst particles were removed from the solution by centrifugation at 12 000 rpm. The crude reaction mixture was then analyzed by GC/MS methods and also by comparison to pure samples of the desired products which were prepared by reacting commercially available toluenediisocyanate with methanol. Figure S7 in the Supporting Information shows some chromatograms illustrating the time conversion as well as the mass spectra of *ortho*-**1**, *para*-**1**, and **2**. The reactions were carried out at least in triplicate. No significant deviations in the conversions and yields among the runs were observed. Only experiments with mass balances ≥ 95 % were considered. Table 1 includes the average values of mass balance, conversion, and yield.

FTIR procedure: FTIR spectra were collected on a BioRad FTS-40 A spectrometer. The infrared cell, connected to a dosing system, was designed to treat the samples in situ under controlled atmospheres and temperatures. The samples were evacuated at 10^{−5} mbar and 373 K for 1 h prior to the adsorption experiments. DMC (2 mbar) and aniline (0.5 mbar) were coadsorbed onto the support surface at room temperature. After reactant adsorption the sample was evacuated to remove the excess of both reactants. Spectra were collected at different temperatures.

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