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Continuous flow carbamoylation of aniline by dimethyl carbonate using a microreactor coated with a thin film of ceria supported gold nanoparticles

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ABSTRACT

Selective carbamoylation of aniline by dimethyl carbonate has been performed under continuous flow using a microreactor having 10 μm microchannels and 4 ml of total volume. Nanoparticulated ceria and gold nanoparticles supported on nanoparticulated ceria that have proved to be highly selective in batch reactions were tested as catalysts. The catalyst coating was deposited as thin film on the stainless steel microreactor plate that was previously activated by heating at 700 °C for 2 h. It was observed that at 120 °C and 5 bar pressure, both catalysts were stable over long times on stream reaching maximum conversions about 35%.

1. Introduction

Aromatic polyurethanes are among the best selling polymers and their production has been continuously growing in the last decade [1,2]. The synthesis of aromatic polyurethanes involves the reaction of polyols with aromatic diisocyanates which are in turn obtained by the reaction of aromatic diamines with phosgene [3]. Phosgene is a highly toxic chemical warfare agent [4,5]. In addition, phosgene is prepared from CO that derives from fossil fuels by steam reforming and water gas shift [6,7]. Due to environmental and societal concerns, there is a strong move for finding suitable replacements to phosgene. One alternative could be the use of dimethyl carbonate (DMC) that by reaction with aromatic amines will render aromatic *O*-methyl carbamates [8–10]. Thermolysis of these aromatic carbamates will render aromatic diisocyanates through an alternative way not involving phosgene. Additionally, if DMC is obtained from CO_2 rather from CO, the whole process will have the extra advantage of being CO_2-neutral since the carbon atom incorporated in the isocyanate group will derive from CO_2 [11–13]. Scheme 1 shows the synthetic route based on DMC compared to the conventional synthesis based on phosgene.

The main problem of using DMC as reagent is its dual behaviour as methylating and carbamoylating agent and the need of developing suitable and selective catalysts for the carbamoylation process [14–18]. In contrast to aliphatic amines, aromatic amines tend to give preferably *N*-methylation when reacting with DMC and, therefore, there is a need of finding heterogeneous and stable selective carbamoylation catalyst for aromatic amines [19,20]. Scheme 2 shows the dual reactivity of DMC when reacting with amines.

Recently we have reported that gold supported on nanoparticulated ceria (Au/CeO_2) is an efficient catalyst to promote the selective *N*-carbamoylation of aromatic amines [21]. The ceria support exhibits an intrinsic catalytic activity towards the carbamoylation of aromatic amines that is enhanced by the presence of gold nanoparticles [21]. The catalyst Au/CeO_2 exhibits a high productivity and working under batch conditions it can be reused without observing any catalytic activity decrease. The efficiency of this catalyst can open an alternative way for the production of aromatic polyurethanes based on DMC.

In the present work we provide a catalytic study under continuous flow of the activity of nanoparticulated CeO_2 and Au/CeO_2 using a microreactor. Continuous flow operation requires the use of highly stable catalysts that do not become deactivated during the course of the reaction. In addition process intensification in where conventional reactors are miniaturized to micro channels should allow reaching the target production minimizing the required reactor volume [22–24]. In this way using a microstructured reactor the maximum production in the minimum volume can be achieved (process intensification) with the additional advantages of having the optimal heat transfer and using the lowest possible catalyst. In the miniaturization of the reactor, the best design should contemplate channels below 1 mm depth, but still sufficiently large to accommodate the solid catalyst bed and allowing the flow of the reaction mixture through it.

In the sequel it will be shown here that using nanoparticulated CeO_2 and Au/CeO_2, carbamoylation of aniline can be carried out with very high selectivity under continuous flow in a microreactor without observing catalyst deactivation at long times on stream.

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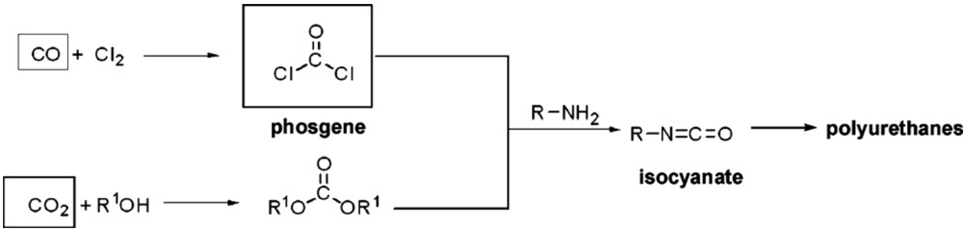
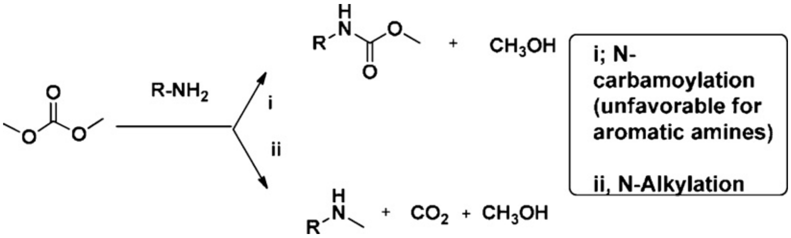


Scheme 1. Synthesis of polyurethanes based on phosgene or organic carbonates.



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

2. Experimental

2.1. Preparation of nanoparticulated ceria

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 $Ce(NO_3)_4$ (0.8 M). The resulting colloidal dispersion of CeO_2 nanoparticles was aged 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 (average particle size 5 nm), a very high surface area (180 $m^2 g^{-1}$) [25].

2.2. Preparation of nanoparticulated ceria supported gold nanoparticles

Au/CeO_2 was prepared using a solution of 200 mg of $HAuCl_4{\cdot}3H_2O$ in 40 ml of deionised 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 CeO_2 (10 g) in H_2O (50 ml). After adjusting again the pH with NaOH 0.2 M, the slurry was left under vigorous stirring at room temperature for 18 h. The Au/CeO_2 solid was then filtered and exhaustively washed with distilled water until no traces of chlorides were detected by the $AgNO_3$ test. The catalyst was dried at room temperature under vacuum. The total Au content of the final catalyst was 0.44% in weight as determined by chemical analysis using X-ray fluorescence comparing the response of the Au/CeO_2 with standards. Under this procedure, 3–4 nm overage gold nanoparticles (average size) supported on CeO_2 are obtained.

2.3. Description of the microreactor

The reactor consists on a stainless steel plate (5 × 10 cm^2) having parallels channels of (10 μm) width. The plate contains in the left and right hand sides triangular inlet and outlet, respectively, that allows the uniform flow through the microchannel system and the collection of the effluents. This simple design has been found to perform adequately in other intensified processes, avoiding preferential path in the flow. The plate is mounted inside a thick stainless steel body (1 cm), the top of which has the inlet and outlet tubes that allows feeding the microreactor and collecting the effluent, respectively. The outlet was connected to a valve having a manometer that keeps the microreactor pressurized (maximum pressure 5 bar), and minimizes the loss of volatile components. The whole microreactor was sealed with an *O*-ring seal spacer that allows the hermetic sealing of the reactor. The upper and lower parts of the reactor are kept tight by eight peripheral Allen knobs. Figs. 1 and 2 show a photograph of the components and assembling of the microreactor.

The microreactor and the Teflon seals are adequate to stand a maximum temperature and pressure of 150 °C and 5 bar, respectively. The total volume of the microreactor was 4 ml. The catalyst was deposited on the reaction plate as a thin film. Prior to deposition of the catalyst layer the reactor plate was heated at 700 °C for 2 h. At this time, activation of the plate can be visually observed by the deep blue color developed on the stain steel during the thermal treatment. When the reactor plate is receptive, the paste containing the catalyst (500 mg containing 1.46 mg of Au) is extended uniformly on the surface using the conventional razor blade procedure. The catalyst paste was prepared by suspending 1 g of the solid catalyst on an acetone solution (20 ml) containing terpineol (10 ml) and ethyl cellulose (0.5 g). The mixture is stirred magnetically overnight at room temperature to obtain a homogeneous paste. After spreading the paste on the receptive plate, the solvent was evaporated at the ambient and the catalyst-coated plate was calcined at 450 °C for 2 h under air to achieve the complete combustion of the organic

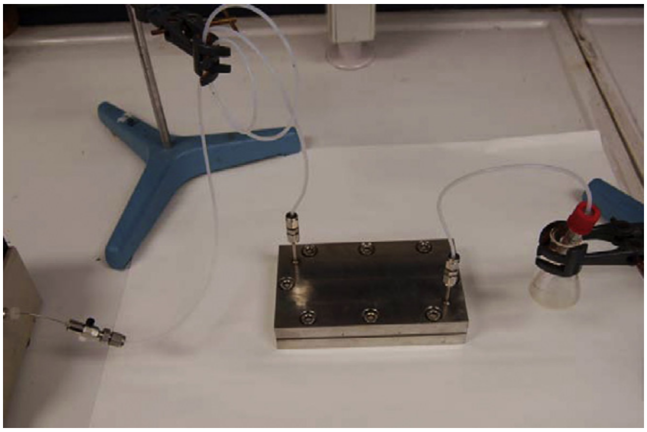


Fig. 1. Photograph of the microreactor used for the continuous carbamoylation of aniline.

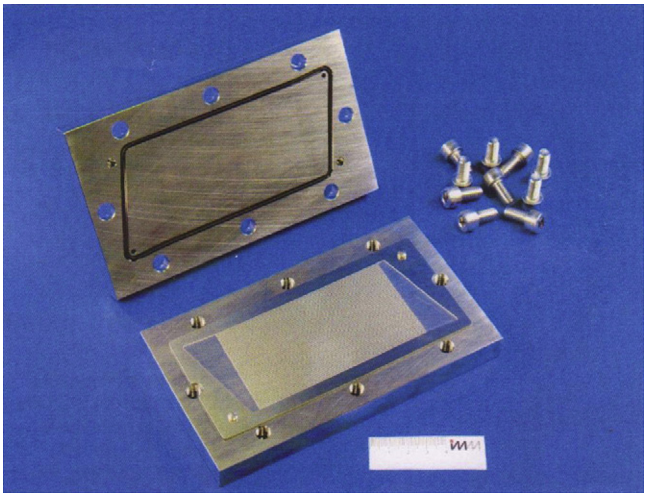


Fig. 2. Parts of the microreactor showing the microchannel plate coated with a thin film of nanoparticulated ceria.

binder. This treatment produces the strong adherence of a mechanically resistant catalyst layer on the reactor plate (see Fig. 2 for an image of the ceria coated plate). The amount of catalyst present on the reaction plate (about 100 mg) was determined knowing the paste that was used in the coating process and also from the increment in weight of the plate. It was estimated that after calcinations the plate contained about 330 mg of Au/CeO_2 that correspond to 1.46 mg of Au.

2.4. Continuous flow carbamoylation of aniline

The required amount of aniline and *n*-dodecane as internal standard were dissolved on the corresponding amounts of DMC and *o*-xylene. The exact amount of reagents and solvents is indicated in the captions of Figs. 3–5. The solutions were introduced in the reservoir of a syringe pump that feeds the microreactor at a constant flow (1 or 2 ml h^{-1} see Figs. 3–5 captions). The reaction mixture from the microreactor was collected in a cold trap. The weight of the aliquots and the time at which each sample was collected were determined. The reaction mixtures were analyzed by GC using a Hewlett Packard instrument using a 30 m 5% crosslinked phenyl methyl silicone column (0.45 mm internal diameter). The identity of the product was determined by co-injection with authentic sample as well as by GC–MS.

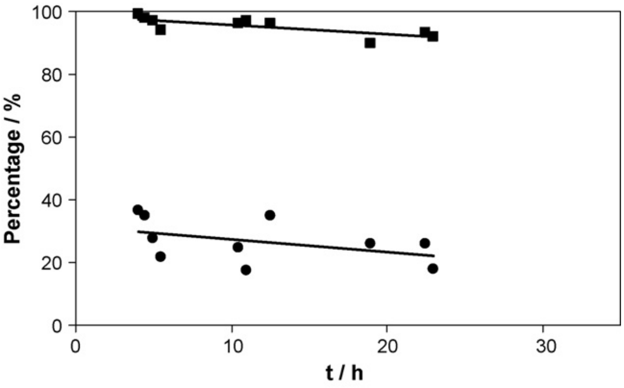


Fig. 3. Time plot conversion (in hours) of aniline (●) and selectivity of *N*-phenyl-*O*-methyl carbamate (■). Reaction conditions; feed: 32.84 g *n*-dodecane as standard, 23.64 g aniline, 56.90 g DMC, 220 g *o*-xylene, 150 °C and flow rate 1 ml h^{-1}. Catalyst: 0.132 g CeO_2, space velocity = 6.41 mmol aniline/h × g cat.

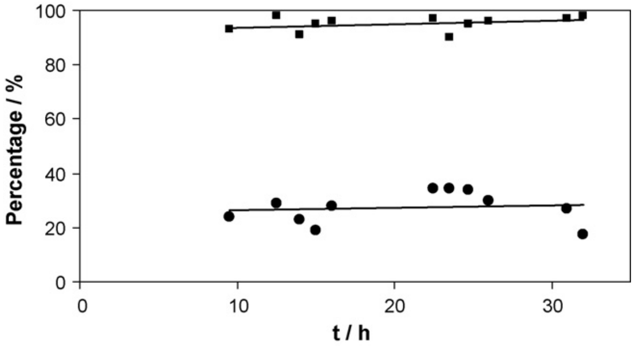


Fig. 4. Time plot conversion (in hours) of aniline (●) and selectivity of *N*-phenyl carbamate (■). Reaction conditions; feed: 31.70 g *n*-dodecane as standard, 42.78 g aniline, 427.6 g DMC, 120 °C and flow rate 2 ml h^{-1}. Catalyst: 0.128 g CeO_2. Space velocity = 14.37 mmol aniline/h × g cat.

3. Results and discussion

The aim of the present work is to obtain data under continuous flow operation of the stability of nanoparticulated CeO_2 and Au/CeO_2 for the reaction of aniline with excess of DMC (Scheme 3) using a microreactor for process intensification.

These two catalysts have shown complete selectivity for carbamoylation of aromatic amines [21], but significant differences in the activity have been determined working under batch conditions. CeO_2 consists on ceria nanoparticles of 5 nm average particle size. Prior work has shown that upon decrease of the particle size in the nanometre range, CeO_2 develops structural defects consisting in framework oxygen vacancies and the coexistence of Ce^{3+} and Ce^{4+} in the framework [26]. The occurrence of oxygen vacancies arising from the nanometre size has been shown to play an important role in catalysis particularly for low temperature CO oxidation and other aerobic oxidations [27,28].

Au/CeO_2 consists on gold nanoparticles (3–4 nm size) homogeneously dispersed on nanoparticulated ceria at a loading of 0.44 wt%. TEM images of CeO_2 and Au/CeO_2 coincide with those that have been previously reported for these materials [29]. It was observed for batch reactions that Au/CeO_2 exhibits higher catalytic

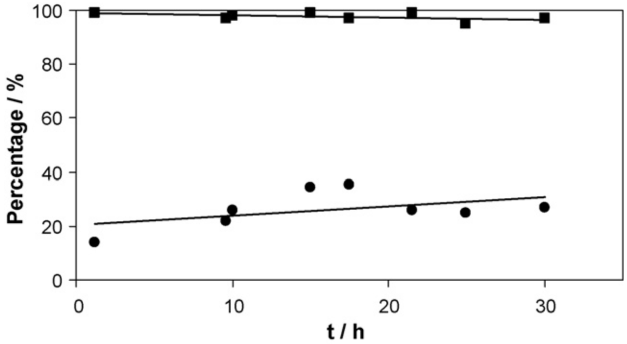
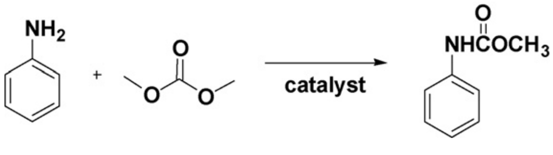


Fig. 5. Time plot conversion (in hours) of aniline (●) and selectivity of *N*-phenyl carbamate (■). Reaction conditions; feed: 31.70 g *n*-dodecane as standard, 42.78 g aniline, 427.6 g DMC, 120 °C and flow rate 2 ml h^{-1}. Catalyst: 0.085 g Au/CeO_2. Space velocity = 21.64 mmol aniline/h × g cat.



Scheme 3. Carbamoylation of aniline by DMC.

activity than plain nanoparticulated CeO_2 probably due to the creation of additional defects, particularly at the gold ceria interface, as well as by the presence of the positive gold atoms mostly located at the corner and edges of the nanoparticles [30]. Using these two catalysts and employing the microreactor shown in Figs. 1 and 2 we have performed the carbamoylation of aniline.

Aniline can be considered as the simplest model of aromatic amines. It has been found that due to the influence of substituents, other industrially relevant aromatic diamines such as 2,4-toluendiamine react faster than aniline [21]. Aniline can also be considered as a model of isomeric bis(aminophenyl)methanes that besides 2,4-diaminotoluene are the amine precursors of isocyanates of large industrial relevance. Obviously, based on the well-known effect of substituents through inductive effect and conjugation, it can be predicted that electron donating substituents increasing the nucleophilicity of the N atom will favour the reaction while electron withdrawing substituents will play the opposite effect. In our study, DMC was used in excess and, therefore, it acts as solvent and reagent. However due to the low boiling point of DMC (90 °C at atmospheric pressure) and the reaction temperature at which carbamoylation is typically carried out in batch reactor (160 °C), we have performed also other tests in which lesser excesses of DMC were used and *o*-xylene was employed as solvent. The aniline conversion over the time on stream (given in hours) and the selective towards *N*-phenyl-*O*-methylcarbamate is plotted in Figs. 3–5.

The only product observed was in all cases the expected *N*-phenyl-*O*-methylcarbamate (Scheme 3), formation of undesired *N*-methylated products being not detected under these conditions. The use of *o*-xylene (boiling point 138.5 °C) as co-solvent has allowed operation of the microreactor at 150 °C without reaching the microreactor limit pressure. This temperature (150 °C) is about the optimal temperature found for batch reactions (160 °C). It has to be noted that due to the dilution of aniline, the space velocity for the experiment using *o*-xylene as co-solvent was lower than that of the other experiments. As it can be seen in Fig. 3 the average conversion using *o*-xylene as solvent was about 30% that is similar to the experiments in where no co-solvent was used and the reaction was carried out at higher space velocity and lower temperature. Moreover, from the conversion/selectivity data obtained it can be seen that the experiment carried out using *o*-xylene as co-solvent and higher reaction temperature exhibits a gradual decay in conversion and selective as a function of the time on stream (Fig. 3). Thus, it can be concluded that no advantage of *o*-xylene dilution and higher reaction temperature is observed in the continuous flow experiment with respect to the aniline conversion.

In fact, Fig. 4 shows that the excess of DMC can compensate the decrease in the activity expected at lower reaction temperatures without noticing any decrease in the aniline conversion that remained slightly below 30% without apparent deactivation even after 34 h time on stream.

The benefits of the presence of gold nanoparticles, even in such small loading on the catalyst, can be observed by the fact that Au/CeO_2 exhibits a 35% average conversion without decay in the catalytic activity, even though the space velocity of the experiment is notably higher than the analogous experiment performed using CeO_2 as catalyst (see Figs. 3–5 captions for the space velocity numbers of each experiment). This increased conversion even for the limited residence time in the microreactor (residence time 2 h) illustrates again the influence of gold nanoparticles boosting the intrinsic catalytic activity of ceria for the selective carbamoylation of aromatic amines. The estimated TON (molecules of carbamate formed per gold atoms) for the catalytic reaction using Au/CeO_2 was about 1500.

In conclusion, the data presented show that CeO_2 and Au/CeO_2 are stable catalysts that can effect the conversion of aniline into the corresponding carbamate under continuous flow operation. One important point of our results is that the transformation can be suitably performed in a microreactor using an appropriate plate coated by a thin film of the catalyst. Catalyst deposition after annealing the stainless steel plate, followed by calcination of the binder renders a catalyst thin film exhibiting an excellent adherence of the solid catalyst bed to the stainless steel plate. Even though the conversion level is moderate and around 35%, we have noticed a significant influence of the presence of gold increasing the activity of ceria. The above data can be used as a base to develop an industrial process for aromatic carbamates that can be important intermediates in a CO_2-neutral route without employing toxic phosgene.

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