Phosgene-free carbamoylation of aniline via dimethyl carbonate*

Sandra Grego, Fabio Aricò, and Pietro Tundo‡

Department of Environmental Science, Informatics and Statistics, Cà Foscari University of Venice, 2137 Dorsoduro, 30123 Venice, Italy

Abstract: The synthesis of *N*-phenylcarbamate from aniline and dimethyl carbonate (DMC) in the presence of homogeneous, supported heterogeneous, and heterogeneous catalysts was investigated in batch conditions. First, a selection of homogeneous catalysts was studied and their reactivity in the same reaction conditions was compared to zinc acetate, a catalyst extensively used for this reaction. Then the best homogeneous catalysts were supported on silica or alumina, and the resulting heterogeneous supported catalysts were tested for the carbamoylation of aniline.

Finally, several heterogeneous catalysts were investigated. Zinc carbonate basic was shown to be the best catalyst, giving quantitative conversion and selectivity for the *N*-phenyl-carbamate. Its catalytic activity was fully investigated taking into account substrate concentration, amount of catalysts, and temperature influence. Zinc carbonate was also shown to be recyclable, once it was recovered from the reaction mixture and calcinated.

Keywords: amines; catalysis; cyclic carbamates; dimethyl carbonate; green chemistry.

INTRODUCTION

Organic carbamates are very versatile compounds widely employed as pesticides, fungicides and herbicides, dyes, pharmaceuticals, cosmetics and in the synthesis of polyurethanes, in addition to being used as protecting groups [1]. Industrially, carbamates are synthesized predominantly through the reaction of the parent amine with phosgene (i.e., chloroformate, eq. 1, Scheme 1) [2]. This process is toxic and produces unwanted waste. Therefore, in recent years, many environmentally benign alternative pathways to carbamates have been investigated, i.e., oxidative carbonylation of amines (eq. 2, Scheme 1), reductive carbonylation of aromatic nitro compounds (eq. 3, Scheme 1), methoxy carbonylation via carbonate chemistry (eq. 4, Scheme 1) [3], and by reaction of urea with symmetrical carbonates (eq. 5, Scheme 1). This latest process is very efficient, although it can be used only when the two components (urea and carbonate) are either both aliphatic or aromatic, limiting the possible number of accessible products [4].

Probably the most promising phosgene-free synthetic approach for carbamoylation of aniline is the one involving dimethyl carbonate (DMC) chemistry. DMC is a green reagent mainly produced in China by insertion of CO_2 into epoxides and cleavage of the resulting cyclic carbonate with methanol [5]. Direct synthesis of DMC from methanol and CO_2 has also been recently reported [6].

Short-chain dialkyl carbonates and, in particular, DMC are renowned for possessing properties of low toxicity and high biodegradability, which make them true green solvents and reagents [7]. DMC
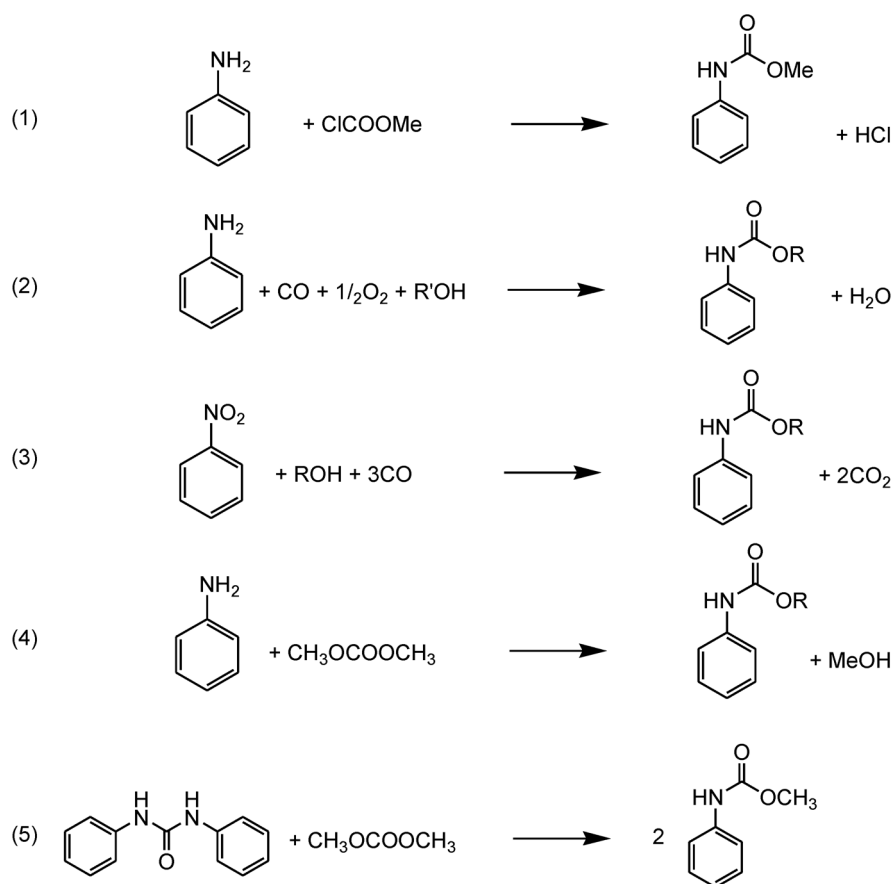
Scheme 1 Synthesis of carbamate via: chloroformate (phosgene) route (eq. 1), oxidative carbonylation (eq. 2), reductive carbonylation (eq. 3), DMC chemistry (eq. 4), and from urea (eq. 5).

has been used as efficient eco-sustainable substitute of the most common carboxymethylating and methylating agents such as phosgene, methyl halides, or dimethyl sulfate. Dialkyl carbonates and, in particular, DMC have shown high selectivity with different monodentate and bidentate nucleophiles acting as carboxymethylating and/or methylating agent [8]. The reactivity of the two electrophilic centers of DMC can be selectively tuned, temperature being the key factor. In fact, usually at reflux temperature ($T = 90$ °C) DMC acts as methoxycarbonylation agent by $B_{Ac}2$ mechanism while at higher temperature ($T > 150$ °C) the methylation reaction occurs via the $B_{Al}2$ mechanism. Both reactions produce as by-product only methanol and eventually CO_2 [8].

Over the last 10 years, reactions between amines and DMC or other symmetrical carbonates have been investigated. In general, the result was the high selective synthesis of monoalkyl, dialkyl derivatives, and in some cases of the related carbamate [9,10]. In most cases, the synthesis of carbamate did not result in atom efficiency owing to the presence of the related alcohol as by-product.

However, recently, there have been reports of several examples of efficient carbamoylation of aniline [11], 4,4'-methylenedibenzenamine [12] (for the synthesis of methylene diphenyl diisocyanate, MDI) and 2,4-diaminotoluene (DAT) (for the synthesis of toluene diisocyanate, TDI) [13] by DMC chemistry employing either homogeneous or supported catalysts.

Among them, an efficient carbamoylation of DAT by Au-catalyzed phosgene-free synthesis has been reported. This approach is particularly interesting as it can be extended to the one-pot process that starting from 2,4-dinitrotoluene leads directly to the polyurethane precursor TDI [14].

Furthermore, the great interest in this research field is clearly demonstrated by the numerous industrial patents involving the use of dialkyl carbonates [15].

In this work, we aim to investigate several homogeneous, supported, and heterogeneous catalysts for the carbamoylation of aniline via DMC chemistry. Our intent was to compare the best known homogeneous catalysts for this reaction under the same conditions. Thus, the reactivity of the best performing catalysts on selected supported materials was investigated so as to overcome the main issue of homogeneous catalysts that are not easily recovered from the reaction mixture. Finally, a selection of heterogeneous catalysts were employed, and the most reactive one, zinc carbonate basic, was further investigated in terms of catalyst amount, molar ratio aniline/DMC, and reaction conditions to achieve the methyl *N*-phenylcarbamate in high yield and short reaction span. The recyclability of zinc carbonate basic was also studied.

EXPERIMENTAL DATA

Materials and data analysis

All the reactions were performed employing DMC dried on molecular sieves 4 Å.

Bases and catalysts were purchased and used without any further purification. Aniline, *N*-methyl *N*-phenylcarbamate, *N*-methyl aniline, *N,N*-dimethyl aniline, and diphenylurea concentration were analyzed by high-performance liquid chromatography (HPLC)-UV using nitrobenzene as internal standard. The HPLC response factor was calculated using a standard mixture of *N*-methyl phenylcarbamate (87.3 % mol) *N*-methyl aniline (12.7 % mol). This standard mixture was prepared, quantified by ^{1}H NMR, and then its related HPLC response factor was calculated.

Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded at 300 MHz NMR.

The supported heterogeneous catalysts were prepared by dissolving the selected metal salt in water. Then alumina or silica was added to the solution, the water was removed by evaporation, and the resulting supported catalyst was dried for 12 h at 90 °C and then calcined at high temperature, i.e., 500 °C. The physical properties of the support materials selected for this study are reported in Table 1.

Table 1 Types of support materials and their physical properties.

Support	Alumina phase	Particle size μm m^2/g	Surface area
Activated carbon		150	n.a.
Alumina activity I, basic		50–1500	n.a.
Alumina nanopowder	γ	00.4–00.47	35–45
Alumina Duralox	γ	n.a.	257
Alumina activated neutral	γ	40	200
Alumina	α	0.1–0.7	9
Alumina fused	α	80–150	n.a.

Typical batch experiment

Batch experiments were conducted in a 200-mL stainless steel pressure vessel equipped with a magnetic stirrer and temperature control system.

In a typical experiment, the reactor was charged with 100 mL solution of aniline and DMC molar ratio 1:10 in the presence of the selected homogeneous, supported, or heterogeneous catalyst. The reaction was monitored by taking sample at time intervals.

Aniline conversion and *N*-phenylcarbamate selectivity were calculated by HPLC measurements using nitrobenzene as internal standard.

RESULTS AND DISCUSSION

Homogeneous catalysts

Preliminary investigations were conducted employing homogeneous catalysts and comparing their reactivity with the one of zinc acetate, extensively investigated for the carbamoylation of aniline [12–15]. Scheme 2 shows the mechanism of carbamoylation of aniline via DMC chemistry. As depicted in Scheme 2, besides methyl *N*-phenylcarbamate **1**, several by-products are formed by reaction of aniline with DMC, i.e., *N*-methyl aniline **4** and *N,N*-dimethyl aniline **5**. Furthermore, the methyl carbamate **1**, once formed, can react further either with DMC to give the methyl *N*-phenylcarbamate **2** or with aniline to form the diphenylurea **3**. It is noteworthy that the reactions leading to the formation of carbamate **1** and urea **3** are equilibrium reactions ($B_{Ac}2$ mechanism), meanwhile the reactions leading to the methyl derivatives **2**, **4**, and **5** are not equilibrium reactions ($B_{Al}2$ mechanism).
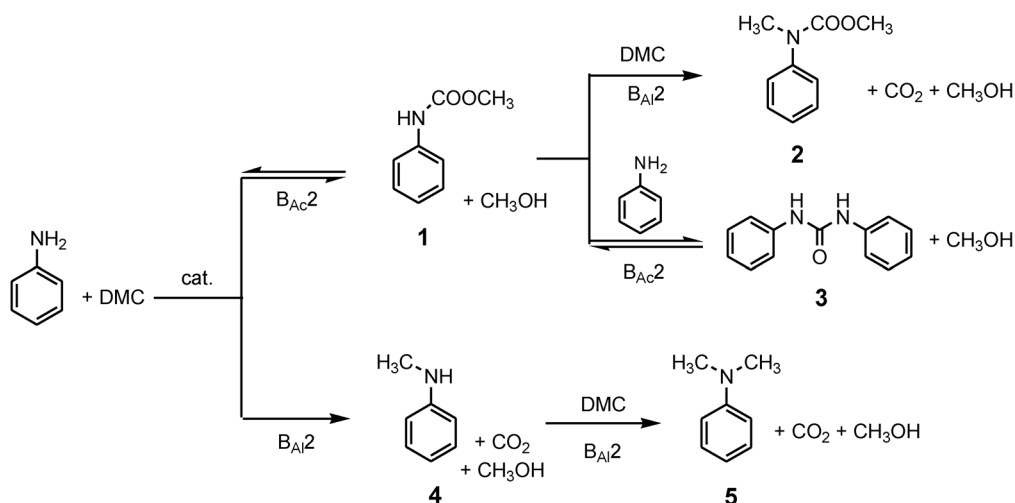
Scheme 2 Synthesis of the methyl *N*-phenylcarbamate **1** by reaction of aniline with DMC. The synthetic pathways leading to the by-products **2–5** are also shown.

In a typical experiment, a solution of aniline and DMC (10 mol equiv), used as solvent and reagent was reacted in an autoclave at 160 °C in the presence of the selected catalyst. The amount of catalyst used was in the range of 0.5–1.6 mol %.

Table 2 shows results achieved employing different homogeneous catalysts. Among the catalysts investigated, the commercially used zinc acetate (Table 2, entry 1) and lead oxide (Table 2, entry 6) resulted in the more efficient ones. In both experiments, aniline was quantitatively converted into the methyl *N*-phenylcarbamate **1**. The reactions catalyzed by cesium carbonate and ytterbium triflate hydrate showed a good conversion of the aniline, but a small selectivity for the carbamate **1** (Table 2, entries 5 and 7). The two titanium catalysts gave very small conversion (Table 2, entries 2 and 3), and dibutyltin dilaurate (DBTDL) gave only a small conversion of the aniline, although increasing the reac-

tion temperature to 180 °C resulted in higher conversion (84 %) and a good selectivity for the carbamate **1** (Table 2, entry 4).

Table 2 Reaction of aniline with DMC (10 mol equiv) in the presence of different homogeneous catalysts in autoclave at 160 °C.

#	Catalyst (% mol)[a]	Time h	Conv. (%)[b]	Me *N*-phenyl carbamate **1** (%)[b]	Other products[b] (%)			
					2	**3**	**4**	**5**
1	Zn(AcO)$_2$·2H$_2$O (1.0)	6	97	96	0	2	2	0
2	Ti(BuO)$_4$ (0.5)	6	22	60	0	0	37	3
3	(C$_5$H$_5$)$_2$Cl$_2$Ti (1.0)	5	11	4	0	1	88	7
4	DBTDL (1.0)	2	11 (84)[c]	55 (76)[c]	0 (0)[c]	19 (4)[c]	26 (14)[c]	0 (5)[c]
5	Cs$_2$CO$_3$ (1.6)	7	94	10	73	0	13	3
6	Pb$_3$O$_4$ (1.6)	5	99	99	0	0	1	0
7	Yb(CF$_3$SO$_3$)$_3$·*x*H$_2$O (1.0)	5	97	39	0	0	9	51

[a]Molar percentage on aniline concentration.
[b]Conversion and selectivity calculated by HPLC measurements using nitrobenzene as internal standard.
[c]After 2 h at 160 °C, the reaction temperature was raised to 180 °C for 3 h.

Heterogenized catalysts

According to the best results obtained for the carbamoylation of aniline employing homogeneous catalysts (Table 2) and to the bibliographic data available, lead, tin, copper, zinc, and bismuth salts were selected to be supported on silica or alumina [11–14]. Supported heterogeneous catalysts were investigated with the intent to easily recover the catalyst at the end of the reaction without using any time-wasting separation and/or purification needed for the homogeneous catalysts.

The detailed list of materials used as catalyst supports and their physical properties are reported in the experimental section.

The supported catalysts were prepared by dissolving the selected metal salts in water, adding the chosen support to the mixture, and then removing the solvent by evaporation. The resulting supported heterogeneous catalysts were calcinated at 500 °C overnight. The final concentration of the metal on the support depended on the solubility of the salt and on the absorption capability of the support.

Results achieved with supported catalysts are summarized in Tables 3 and 4. Experiments were carried out at 160 °C (Table 4) or 180 °C (Table 3), with a catalyst amount ranging from 1.0 to 3.2 mol %. Reactions performed at 180 °C showed in general a small conversion and/or a small selectivity for carbamate **1** (Table 3, entries 1–7). The best result was obtained employing lead salt supported on α-alumina (Table 3, entry 7).

Reactions performed at 160 °C (Table 4) showed a similar pattern as lead supported either on α- or γ-alumina was the most reactive catalyst among the ones investigated. It is noteworthy that the support material played an important role. In fact, among the tested support materials only a few gave good carbamate selectivity: two were α-alumina and one was γ-alumina nanopowder, maybe because all of them have a low absorption capacity (low surface area), this ensured a good distribution of the catalyst over the support surface.

Table 3 Reaction of aniline with DMC (10 mol equiv) in the presence of a supported catalysts at 180 °C in autoclave.

#	Supported het. catalyst (% mol)[a]	Time h	Conv. (%)[b]	Methyl N-phenyl carbamate **1** (%)[b]	Other products[b] (%)			
					2	**3**	**4**	**5**
1	Bi/act. carbon (1.8)	2.5	82	61	0	9	20	10
2	Cu 4.1 % on Al$_2$O$_3$ α[c] (1.6)	4.5	36	31	0	10	43	16
3	Sn 6.7 % on Al$_2$O$_3$ α[c] (1.6)	3.3	18	11	0	11	65	13
4	Zn het. 7.5 % on SiO$_2$ (3.2)	2.3	83	55	0	2	27	15
5	Zn[d] 7.7 % on Al$_2$O$_3$ α[c] (1.6)	3	25	24	0	23	44	8
6	Zn[e] 3.7 % on Al$_2$O$_3$ α (1.6)	3.6	26.5	22	0	17	48	12
7	Pb 10 % on Al$_2$O$_3$ γ (1.6)	3	51	59	0	10	24	7
8	Pb 5.4 % on Al$_2$O$_3$[c] α (1.0)	3.5	99	94	2	0	1	2

[a]Mol % on aniline concentration.
[b]Conversion and selectivity calculated by HPLC measurements using nitrobenzene as internal standard.
[c]Fused alumina.
[d]From ZnCl$_2$.
[e]From ZnAcO.

Table 4 Reaction of aniline with DMC (10 mol equiv) in the presence of a supported catalysts at 160 °C in autoclave.

#	Supported het. catalyst (% mol)[a]	Time h	Conv. (%)[b]	Methyl N-phenyl carbamate **1** (%)[b]	Other products[b] (%)			
					2	**3**	**4**	**5**
1	Bi 18 % on Al$_2$O$_3$ α[c] (1.8)	6	48	48	0	34	16	2
2	Zn het. 7.5 % on SiO$_2$ (1.0)	7	60	54	0	10	29	7
3	Zn 10 % on Al$_2$O$_3$ α[d] (1.9)	5	36	36	0	20	37	7
4	Pb het. 8.5 % on SiO$_2$ (1.0)	7	60	68	0	10	19	2
5	Pb on basic Al$_2$O$_3$[d] (1.6)	7	54	54	0	21	21	4
6	Pb on Al$_2$O$_3$ neutral γ (1.6)	6.5	56	52	0	28	17	4
7	Pb 8.4 % on Al$_2$O$_3$ γ[e] (1.6)	6	98	99	0	0	1	0
8	Pb 9 % on Al$_2$O$_3$ α (1.6)	4	99	97	1	0	1	1

[a]Mol % on aniline concentration.
[b]Conversion and selectivity calculated by HPLC measurements using nitrobenzene as internal standard.
[c]Fused alumina.
[d]Alumina brockman activity I, basic.
[e]Nanopowder alumina.

Heterogeneous catalysts

In order to complete the screening on the best catalysts for the carbamoylation of aniline, several heterogeneous catalysts were investigated. Table 5 shows the results achieved by reacting aniline with DMC (10 mol equiv) at 160 °C in the presence of catalytic amount of different insoluble salts, mainly carbonates.

Both zinc and lead carbonate basic (Table 5, entries 1 and 2) gave good results in terms of selectivity and conversion. Lead carbonate also gave quantitative conversion and selectivity for the methyl N-phenylcarbamate **1**. On the other hand, the reactions carried out employing bismuth carbonate, copper carbonate, and zinc phosphate resulted in small conversion and negligible carbamate selectivity (Table 5, entries 3–5) even at higher temperatures, i.e., 180 °C (Table 5, entries 3 and 4). It is noteworthy that zinc phosphate was shown to be very selective for the monomethylation of the aniline.

Among the tested catalysts, zinc carbonate basic resulted as the most reactive for the N-carbomoylation of aniline; thus, it was investigated in more detail in order to maximize both substrate con-

version and product selectivity. In particular, the effect of aniline concentration, the amount of catalyst, and the temperature were investigated. Finally, the recycling of the catalyst zinc carbonate basic was also studied.

Table 5 Reaction of aniline with DMC (10 mol equiv) in the presence of different heterogeneous catalysts in autoclave at 160 °C.

| #	Catalyst (% mol)[a]	Time h	Conv. (%)[b]	Me N-phenyl carbamate **1** (%)[b]	Other products[b] (%)			
					2	**3**	**4**	**5**
1	$[ZnCO_3]_2 \cdot [Zn(OH)_2]_3$ (1.6)	5	96	94	0	3	3	1
2	$(PbCO_3)_2 \cdot Pb(OH)_2$ (1.6)	4	99	99	0	0	1	0
3	$(BiO)_2CO_3$ (1.6)	2	11 (30)[c]	45 (30)[c]	0 (0)[c]	31 (28)[c]	24 (36)[c]	0 (6)[c]
4	$Zn_3(PO_4)_2$ (1.6)	1	2 (16)[c]	13 (1)[c]	0 (0)[c]	0 (0)[c]	87 (81)[c]	0 (18)[c]
5	$CuCO_3 \cdot Cu(OH)_2$ (3.2)	3	12	53	0	17	30	0

[a]Mol % on aniline concentration.
[b]Conversion and selectivity calculated by HPLC measurements using nitrobenzene as internal standard.
[c]Raising the temperature at 180 °C for 3 h.

Zinc carbonate basic: Aniline/DMC molar ratio

The effect of aniline concentration in the reaction mixture is reported in Fig. 1.

Both conversion and selectivity increased in diluted solution of aniline (aniline/DMC 1/10 and 1/20 molar ratio). In particular, when aniline/DMC molar ratio was 1/20 and 1/10 there was only a small difference in terms of conversion and selectivity for the carbamate **1**, 99 and 94 %, respectively. On the other hand, when the concentration of aniline in the reaction mixture was higher (i.e., aniline/DMC molar ratio ¼), the carbamate selectivity decreased (82 %) owing to the formation of the *N*-methyl aniline (10 %) and diphenyl urea (9 %).
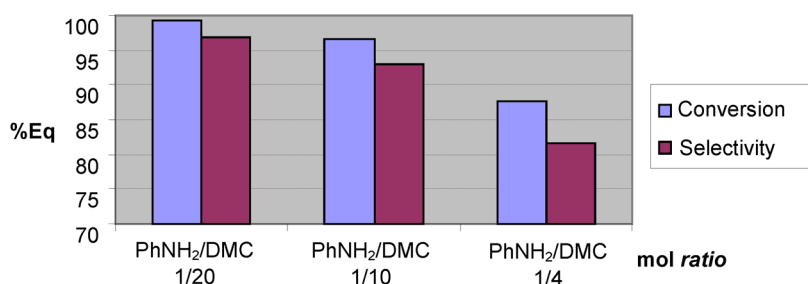

Fig. 1 Effect of aniline concentration on aniline conversion. T = 160 °C in autoclave after 7 h, cat. = 3.2 mol %.

Zinc carbonate basic: Amount of catalyst

The effect of catalyst content on aniline conversion and carbamate selectivity at 160 and 180 °C was also investigated. Results collected are reported in Fig. 2.

At 160 °C, the conversion of aniline and the selectivity for the carbamate **1** increased when the molar percentage of the catalyst was incremented from 0.8 to 1.6 mol %. Then, increasing further the amount of catalyst did not affect significantly the conversion or the selectivity.

When the reaction was carried out using 0.8 mol % of catalyst at 180 °C, the conversion of the substrate was higher than the one observed 160 °C. However, increasing the amount of catalyst affects the reaction outcome in a negligible way. It is noteworthy that in all the experiments urea content was smaller at 180 °C with respect to 160 °C.
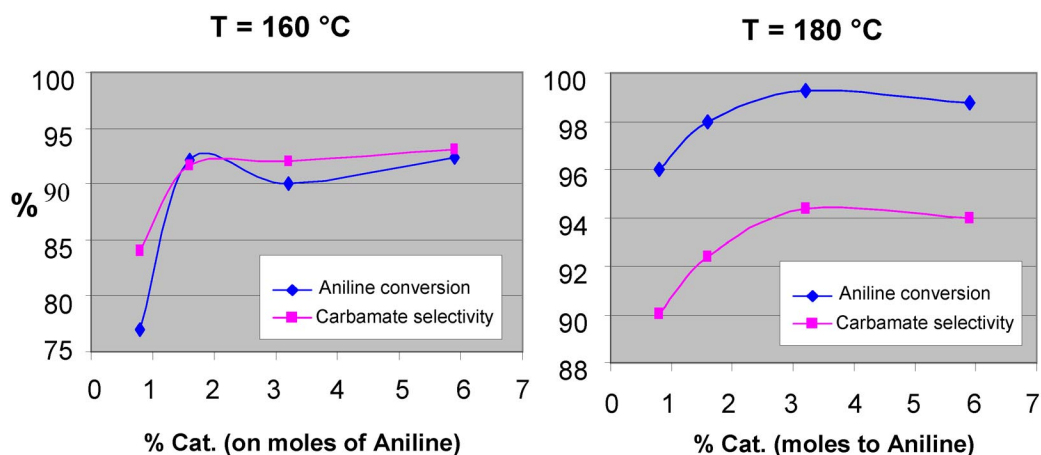
T = 160 °C

T = 180 °C

Fig. 2 Effect of the amount of catalyst on the formation of the carbamate **1** at $T = 160$ °C and $T = 180$ °C in autoclave. Aniline/DMC molar ratio 1/10; reaction time 5 h.

Zinc carbonate basic: Temperature effect

The effect of the temperature at different catalyst content was also evaluated. Results are reported in Table 6.

Table 6 Reaction of aniline with DMC (10 mol equiv) in the presence of $[ZnCO_3]_2 \cdot [Zn(OH)_2]_3$ in autoclave at different temperatures and catalyst amounts.

#	$[ZnCO_3]_2 \cdot [Zn(OH)_2]_3$ (% mol)[a]	Temp.	Conv. (%)[b]	Methyl N-phenyl carbamate **1** (%)[b]	Other products[b] (%)			
					2	**3**	**4**	**5**
1	0.8	160	76	85	0	8	6	1
2	0.8	180	96	90	0	2	6	3
3	1.6	160	94	93	0	4	4	0
4	1.6	180	98	92	0	1	4	2
5	3.2	160	93	93	0	4	3	0
6	3.2	180	99	94	0	1	3	2
7	3.2	200	100	93	2	1	4	3
8	5.9	140	75	90	0	7	3	0
9	5.9	160	92	91	0	4	4	1
10	5.9	180	99	94	0	1	3	2

[a]Mol % on aniline concentration.
[b]Conversion and selectivity calculated by HPLC using nitrobenzene as internal standard.

When an amount of 0.8 mol % of catalyst was used, the reaction was more efficient in terms of conversion and selectivity operating at higher temperature, i.e., 180 °C (Table 6, entries 1 and 2). In the reactions where 1.6 or 3.2 mol % of zinc carbonate basic was used, the increase of temperature did not affect significantly the conversion of the aniline, neither the selectivity for the carbamate, although the best results were achieved always at 180 °C (Table 6, entries 3–7). It is noteworthy that carrying out the reaction at higher temperature (i.e., 200 °C; Table 6, entry 7), carbamate **1** selectivity decreased owing to the formation of N-methyl carbamate as its formation is favored at high temperature. Finally, employing 5.9 mol % of catalyst at 140 °C (Table 6, entry 8) resulted in a moderate conversion of aniline; increasing the temperature at 160 °C showed a better conversion and selectivity (Table 6, entry 9), but

a further raise of the reaction temperature at 180 °C did not improve the reaction outcome (Table 6, entry 10).

Considering all the experiments performed at different temperatures and catalyst amount, the best results were achieved operating at 180 °C in an amount of catalyst >3.2 mol %.

Zinc carbonate basic: Catalyst recycling

Zinc carbonate basic is nearly insoluble in the reaction mixture, therefore, it can be easily separated by filtration and reused. This is clearly an advantage compared to homogeneous catalyst.

In order to study the recycling of the catalyst, zinc carbonate was recovered at the end of a carbamoylation reaction (carried out at 160 °C) by filtration. It was dried at 90 °C overnight, and experiments with this recycled catalyst were performed.

Figure 3 shows the results obtained for the carbamoylation of aniline in the presence of 1.6 mol % of catalyst at 160 °C with fresh catalyst and with a recycled one.

The recycled zinc carbonate basic was almost as efficient as the fresh one. However, if the catalyst is reused for the second time both conversion and selectivity moderately decreased. Probably reactivating the catalyst at higher temperature would be advisable.
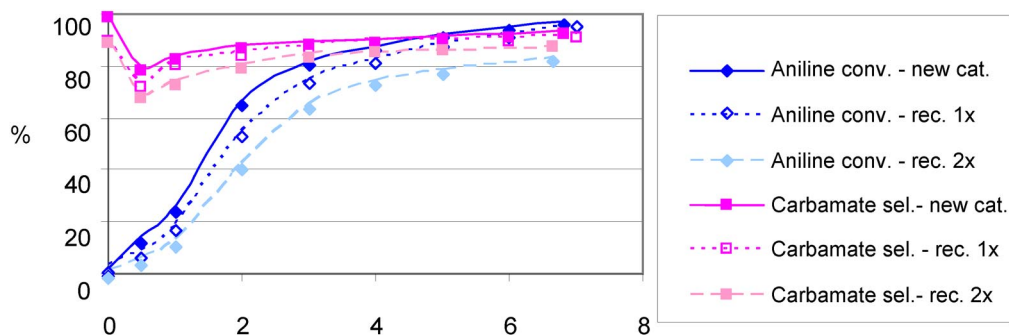
Fig. 3 Reactivity of recycled catalyst. Cat. amount = 1.6 mol % on moles of aniline, $T = 160$ °C, aniline/DMC 1/10 mol ratio.

CONCLUSIONS

Several homogeneous, heterogenized, and heterogeneous catalysts were investigated for the synthesis of *N*-phenylcarbamate **1**. Among the studied homogeneous catalysts, only lead oxide showed a reactivity comparable to zinc acetate. Thus, lead oxide and a selection of other homogeneous catalysts were supported on silica or alumina, and the reactivity of the resulting heterogeneous supported catalysts was investigated at different temperatures. Among them, lead salt supported on alumina was once again the most active in terms of conversion and selectivity for *N*-phenylcarbamate **1**.

Several heterogeneous catalysts were tested in order to study their reactivity. Zinc carbonate basic was shown to be the best catalyst giving quantitative conversion and selectivity for the carbamate **1**. Its catalytic activity was fully investigated, taking into account substrate concentration, amount of catalysts, and temperature influence. Its reactivity was comparable with the extensively investigated zinc acetate. It is noteworthy that compared to zinc carbonate, zinc acetate has the disadvantage of being a homogeneous catalyst and thus difficult to separate from the reaction mixture, and it also forms as unwanted by-product methyl acetate. On the other hand, zinc carbonate basic was easily recovered at the end of the reaction, and, after calcination, it can be efficiently reused. Furthermore, in the zinc carbonate-catalyzed reaction, the formed carbamate **1** can be recovered by evaporation of the solvent without any wasted time and/or expensive purification.

Following these promising results, carbamoylation of aniline was investigated in continuous-flow conditions.

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