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Nitrobenzene carbonylation in the presence of $\text{PdCl}_2/\text{Fe}/\text{I}_2$ and $\text{PdCl}_2\text{Py}_2/\text{Fe}/\text{I}_2$ systems

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Abstract

The new catalytic system $\text{PdCl}_2/\text{Fe}/\text{I}_2/\text{Pyridine}$, active in nitrobenzene carbonylation to ethyl phenylcarbamate (EPC) is presented. For the catalyst composition determined by the following ratio: 0.17/10/1.4/12.4 of its components respectively, at 180°C; under initial CO pressure = 4 MPa, after 2 h, a nitrobenzene conversion reached 99.6%, the percentages of the products obtained were: 83.4% EPC and 14% aniline (NB/Pd = 540).

Influence of initial CO pressure, reaction temperature, reaction time and the catalyst composition on the reaction products, were established. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Nitrobenzene carbonylation; Palladium catalysts; Urethanes

A catalytic reductive carbonylation of nitro compounds to aromatic isocyanates and urethanes is the subject of numerous studies of both an academic and commercial interests [1,2]. In the studies palladium catalysts are primarily used. These are, in the first place, palladium complexes with tertiary amines, and are modified by Lewis acids added [3–5] and the palladium complexes with P/N bidentate ligands, which exhibit a catalytic activity with no addition of co-catalysts [6–10].

In this communication, we present a new $\text{PdCl}_2/\text{Fe}/\text{I}_2$ catalytic system [11] which shows a high activity in the reaction of reduction of aniline with carbon monoxide and water [12]. In this catalytic system iron powder and iodine are the co-

catalysts in place of a Lewis acid that is typically added. The reaction was carried out in a 200-ml steel autoclave applying the following conditions: catalyst $\text{PdCl}_2/\text{Fe}/\text{I}_2 = 0.17:10:0.4$ mmol; 6.2 mmol pyridine; 81 mmol nitrobenzene; 20 ml ethanol (as solvent and reagent); initial CO pressure = 4 MPa; reaction temperature = 180°C; reaction time 120 min. Ratio of nitrobenzene:ethanol = 1:4. Only for the catalytic system shown in Table 3 entry 5, toluene was used as solvent. The yield was calculated from the GC data, (using a Hewlett-Packard model HP6890 gas chromatograph).

Among the reaction products of the nitrobenzene carbonylation in the presence of the catalyst used are: ethyl phenylcarbamate (EFC) and aniline as a by-product (the typical EFC/aniline ratio is 5:1), as well as traces of: diphenylurea, 2-methylcholine, diphenyldiazene, diphenyldiazene oxide, benzene

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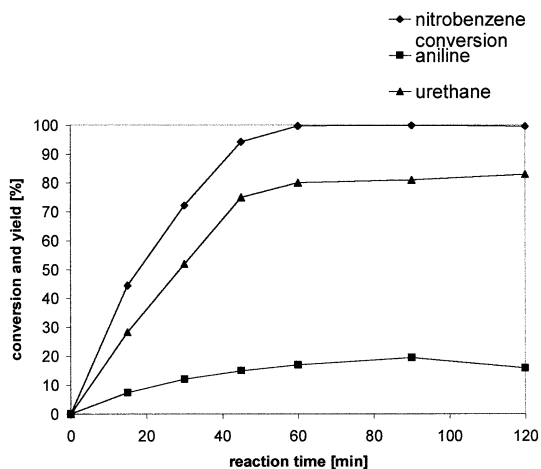


Fig. 1. Nitrobenzene conversion and yield of the carbonylation reaction products vs. time.

azide, and ethoxyaniline. The trace by-products total 1% or less. Aniline is produced here in a nitrobenzene hydrogenation reaction by means of the hydrogen abstracted from ethanol (acetic aldehyde was determined in the reaction gaseous products). The action of alcohol as a nitrobenzene reducer during the carbonylation reaction evidenced also as acetic aldehyde creation, has been described earlier by Liu and Cheng [13]. Ethanol is also consumed in ethyl phenylcarbamate formation.

Shown in Fig. 1 is the variation of nitrobenzene conversion and the carbamate and aniline yields during the reaction. As the reaction proceeds, the aniline yield varies to a minor degree, whereas the carbamate yield rises significantly. This suggests that aniline undergoes a consecutive reaction of carbonylation to carbamate. The aniline carbonylation in an iodine-containing system was observed earlier [14]. For these reaction conditions the products are obtained in maximum yields after a reaction time of about 1 h.

Variation in the carbonylation reaction yield as a function of the initial carbon monoxide pressure is illustrated in Fig. 2. At low carbon monoxide initial pressures (2 MPa), aniline accounts for 31% in the reaction products and lowers to 16% for the pressure equal to 4 MPa. A rise in this pressure results in a substantial increase in the carbamate yield. The results confirm the suggestion that aniline undergoes carbonylation to carbamate in the system studied. An

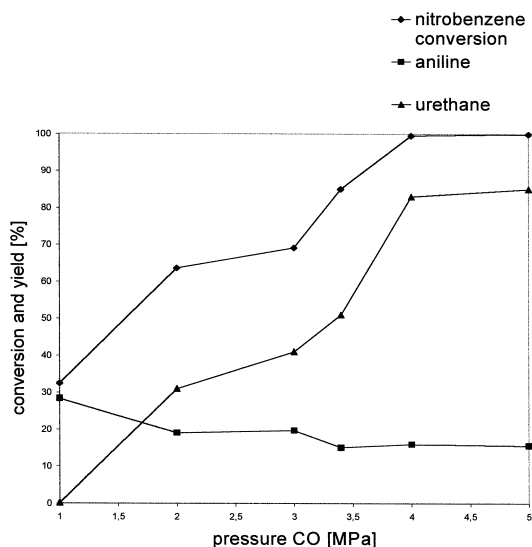


Fig. 2. Nitrobenzene conversion and yield of the carbonylation reaction product vs. initial CO pressure.

increased CO pressure also favours this in the system.

The reactions under discussion are affected by temperature (Fig. 3). At 60°C, at a 42.9% nitrobenzene conversion, the reaction proceeds to form some intermediates, the identification of which has not

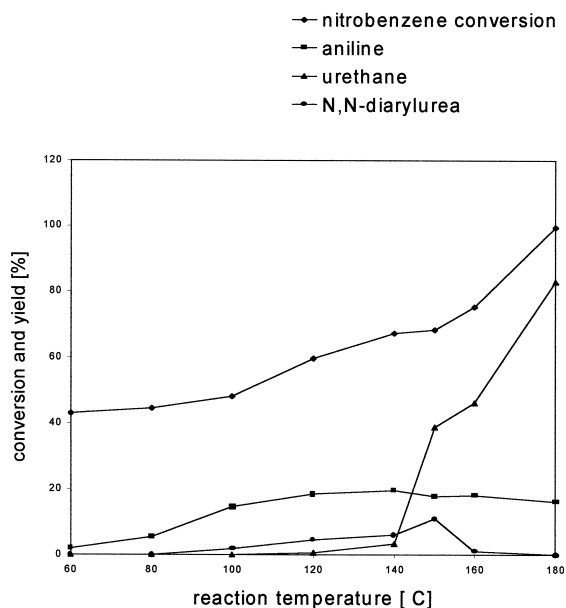


Fig. 3. Nitrobenzene conversion and products yield vs. carbonylation reaction temperature.

Table 1
Effect of iodine compounds on the nitrobenzene carbonylation reaction

No.	Catalyst (g)	Co-catalyst (g)	Solvent (g)	Nitrobenzene conversion (%)	Selectivity (%)	
					Aniline	Ethyl phenyl-carbamate
1	PdCl ₂ (0.03)	Fe (0.5), I ₂ (0.1), PY (0.5)	EtOH (20)	99.6	16.0	83.4
2	PdCl ₂ , (0.03)	Fe (0.5), KI (0.25), PY (0.5)	EtOH (20)	28.5	33.5	76.3
3	PdCl ₂ (0.03)	Fe (0.5), NaI (0.25), PY (0.5)	EtOH (20)	1.8	57	13.8
4	PdCl ₂ (0.03)	Fe (0.5), EtI (0.5), PY (0.5)	EtOH (20)	59.9	23.8	60.7
5 ^a	PdCl ₂ (0.03)	PY (0.5)	EtOH (20)	trace	trace	0
6	–	Fe (0.5), I ₂ (0.1), PY (0.5)	EtOH (20)	0	0	0

^aWith teflon jacket autoclave.

been done. In the products, there is only 5% of aniline and no main product, EPC. As the temperature is raised to 80°C, EPC is already formed, and the aniline content in the reaction products rises. They account for 7% of the products. The nitrobenzene conversion increases insignificantly. This suggests that, at that temperature, the main process occurring in the system is the transformation of the intermediates into aniline and EPC, which just starts forming. As the temperature is raised to 100°C, diphenylurea (DPU) also appears in the products, accompanied by a slight rise in aniline and EPC quantity. A significant rise in the EPC yield is noted at 150°C and further rise in yield of DPU, which is a product of the reaction of aniline with nitrobenzene and carbon monoxide [15]. This is a likely explanation why the aniline content in the reaction products is reduced. A further rise of the reaction temperature to 180°C yields a further increase in the EPC content accompanied by a drop in the amount of the by-products formed. This is evidence that at that temperature the by-products are rapidly converted to the main reaction products.

Reviewed in Table 1 are the catalytic systems in which iodine is present in various compounds. The iodine compounds studied may be arranged in the order of their growing activating role in the catalytic system, viz.: I₂ > C₂H₅I > KI ≫ NaI. In the case of these catalysts, the amount of aniline in the reaction products increases with the declining of the nitrobenzene conversion; when NaI is the iodine source, four times more aniline than the carbamate is formed. The systems PdCl₂/PY and Fe/I₂/PY it means the studied systems without iron and palladium respectively gave only traces of the products — entries 5,6.

The effect of the amount pyridine used as a co-catalyst on the carbonylation reaction is shown in Table 2. In the reactions corresponding to items 1 through 3 of line pyridine was added into the reaction mixture as an independent component of the system, whereas in the reactions corresponding to items 4 though 6 of line the pyridine bonded in the previously synthesized palladium chloride complex was used.

Catalyst PdCl₂(pyridine)₂ (I) used in equimolar quantities as concerns the amount of palladium to the

Table 2
The effect of pyridine quantity on the nitrobenzene carbonylation reaction

No.	Catalyst (g)	Co-catalyst (g)	Solvent (g)	Nitrobenzene conversion (%)	Selectivity (%)	
					Aniline	Ethyl phenyl-carbamate
1	PdCl ₂ (0.03)	Fe (0.5), I ₂ (0.1), PY (0.5)	EtOH (20)	99.6	16.0	83.4
2	PdCl ₂ ² (0.03)	Fe (0.5), I ₂ (0.1), PY (0.5)	EtOH (20)	54.3	12.0	63.5
3	PdCl ₂ (0.03)	Fe (0.5), I ₂ (0.1), PY (1.0)	EtOH (20)	81.1	7.0	86.2
4	PdCl ₂ PY ₂ (0.06)	Fe (0.5), I ₂ (0.1), PY (0.5)	EtOH (20)	94.3	7.0	89.5
5	PdCl ₂ PY ₂ ³ (0.06)	Fe (0.5), I ₂ (0.1), PY (0.5)	EtOH (20)	46.4	15.6	62.2
6	PdCl ₂ PY ₂ (0.06)	Fe (0.5), I ₂ (0.1)	EtOH (20)	23	25	75

^aReaction time 15 min.

Table 3

Effect of the nitrobenzene carbonylation conditions on the selectivity of the by-product aniline formed

No.	Catalyst (g)	Co-catalyst (g)	Solvent (g)	Nitrobenzene conversion (%)	Selectivity %	
					Aniline	Ethyl phenyl-carbamate
1	PdCl ₂ (0.1)	Fe (0.5), I ₂ (0.2), PY (0.5)	EtOH (20)	99.7	12.3	87.7
2	PdCl ₂ ^a (0.1)	Fe (0.5), I ₂ (0.2), PY (0.5)	EtOH (20)	100	4.0	96.0
3	PdCl ₂ (0.1)	Fe (0.5), I ₂ (0.1), PY (0.5)	EtOH (20)	99.7	21.8	79.0
4	PdCl ₂ (0.03)	Fe (0.5), I ₂ (0.1), PY (0.5)	EtOH (20)	99.6	16.0	83.4
5	PdCl ₂ (0.03)	Fe (0.5), I ₂ (0.1), PY (0.5)	EtOH (6) toluene (14)	33.9	33.3	44.7

^aInitial CO pressure = 5 MPa.

PdCl₂-containing catalyst affords a similar final nitrobenzene conversion with a better selectivity towards EPC (items 1,4), compared to the previous system. It will be noted that at low nitrobenzene conversions (a short reaction time) in the presence of catalyst I a similar selectivity is observed as for the PdCl₂ system (items 2, 5 of lines, Table 2). The carbonylation reaction in the presence of the PdCl₂ system in which standard Fe and I₂ amounts were used, yet with no addition of pyridine, proceeds with a low nitrobenzene conversion and a relatively high aniline quantity in the products (item 6). In the reactions in which pyridine was used in excess, aniline was found to be formed in a lower quantity (down to 7%, item 3), compared with 16% (item 1), with a concomitant decline in nitrobenzene conversion.

The effect of various reaction parameters on selectivity towards the aniline formed as a by-product is shown in Table 3. A higher palladium chloride content in the catalyst results in a higher aniline amount and a lower carbamate yield (items 3 and 4). A higher iodine content in the catalyst results in a higher carbamate amount and a lower aniline yield (items 1 and 3). An initial CO pressure increased to 5 MPa results in an enhanced carbamate yield at the expense of aniline (item 2). The carbonylation reaction was made to stop, when the quantity of ethanol, which is a hydrogen donor, was reduced. In this case the nitrobenzene conversion dropped from 99.6 to 33.9% at a concomitant unfavourable ratio of products of AN: EPC = 1:1.3 (item 5).

The results obtained indicate that the optimum reaction conditions for nitrobenzene carbonylation to phenylcarbamate are those given below.

- In the presence of PdCl₂/Fe/I₂/Py catalyst, its composition is determined by the following ratio: 0.17/10/0.4/6.2; 180°C; initial CO pressure = 4 MPa, reaction time 2 h. For these conditions, at a nitrobenzene conversion = 99.6%, the percentages of the products obtained are: 83.4% EPC and 14% aniline (NB/Pd = 540).

- In the presence of PdCl₂Py₂/Fe/I₂/Py catalyst, its composition is determined by the following ratio: 0.17/10/0.4/6.2; 180°C; initial CO pressure = 4 MPa, reaction time 2 h. For these conditions at a nitrobenzene conversion = 94.3%, the percentages of the products obtained are 89.5% EPC and 7% aniline (NB/Pd = 540).

Acknowledgements

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