Communication

Pd Nanoparticles and Mixture of $CO_2/CO/O_2$ Applied in the Carbonylation of Aniline

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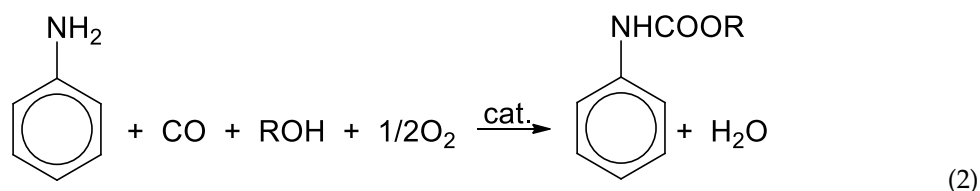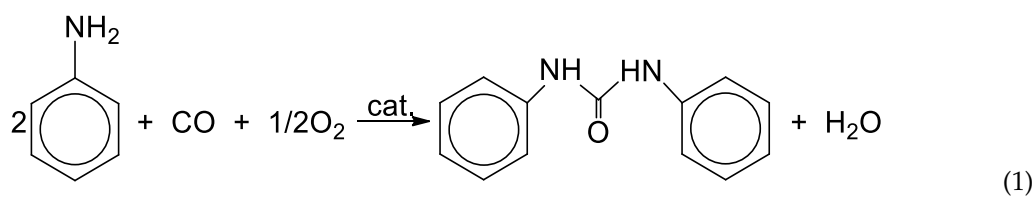
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Abstract: CO_2 is a compound of high stability which proves useful in some organic syntheses as a solvent or component decreasing explosivity of gases. It is also a good carbonylating agent for aliphatic amines although not for aromatic ones, the latter being carbonylated with phosgene or, as in our previous works, with CO/O_2 in the presence of Pd(II) complexes. In this work we have used the mixture of CO/O_2 and CO_2 for carbonylation of aniline to N,N'-diphenylurea. After optimization of the reaction conditions (56% of CO_2 in CO_2/CO mixture) we studied the activity of three kinds of pre-catalysts: (a) Pd(II) complexes, (b) Pd_{black}, and (c) palladium nanoparticles (PdNPs) in the presence of derivatives of pyridine (X_nPy). The highest conversion of aniline (with selectivity towards N,N-diphenylurea ca. 90%) was observed for PdNPs. The results show that catalytic cycle involves Pd(0) stabilized by pyridine ligand as active species. Basing on this observation, we put the hypothesis that application of PdNPs instead of Pd(II) complex can efficiently reduce the reaction time.

Keywords: Palladium; nanoparticles; carbonylation; aniline; carbon monoxide; carbon dioxide

1. Introduction

Environment-friendly organic synthesis is the main challenge of modern science in order to meet the objectives of sustainable development. Among many types of functionalization, insertion of a single carbonyl group into an organic molecule plays a special role due to large-scale demand for carbonyl compounds [1,2]. Excellent examples of products (both commodities and specialty chemicals) with carbonyl groups are urea derivatives, widely used in modern chemical industry— they find application in the production of pesticides (herbicides, fungicides), resin precursors, and fiber dyes [3,4], as well as antiviral and anticancer agents and other pharmaceuticals [4–8]. Numerous derivatives of ureas—including isocyanates and carbamates—are employed in syntheses of adhesives, varnishes, rubbers, paints, and polyurethane foams [9]. Unfortunately, dominating technologies of production of diphenylureas from aromatic amines are based on the phosgene method [9,10], and the real challenge in this sector of industry is to replace them by phosgene-free methods. The most common approaches involve less environmentally harmful carbonylating agents such as CO or alkyl carbonates [1,3,5,11–13], including carbonylation performed in beneficial nonconventional solvents such as ionic liquids [12,13]. The main limitation of CO-based methods is the high pressure applied.

Over the past few years, our studies have been focused on the carbonylation of aromatic nitrocompounds and amines by CO in the presence of the $PdCl_2(X_nPy)_2/Fe/I_2/X_nPy$ catalytic system, where Py = pyridine, X = Cl or CH_3, n = 0–2 [14–17]. We have successfully optimized the reaction conditions and proposed detailed mechanisms for carbonylation of aniline (AN) to N,N'-diphenylurea (DPU, equation 1), or to ethyl N-phenylcarbamate (EPC, Equation (2)), by CO/O_2.

$$2 \ \underset{NH_2}{C_6H_5} + CO + 1/2O_2 \xrightarrow{cat.} \underset{NH \quad HN}{\underset{O}{C_6H_5 - C - C_6H_5}} + H_2O \tag{1}$$

$$\underset{NH_2}{C_6H_5} + CO + ROH + 1/2O_2 \xrightarrow{cat.} \underset{NHCOOR}{C_6H_5} + H_2O \tag{2}$$

Processes presented by Equations (1) and (2) involve mixture of CO (a common source of carbonyl group) and O_2 (oxidizing agent), which is potentially explosive in a wide range of concentrations: 16.7–93.5% (under atmospheric pressure and at 18 °C) [18,19]. Therefore, strategies of eliminating or replacing hazardous substrates with safer and less expensive compounds are actively researched [20], and introduction of carbon dioxide to gaseous components is one of such approaches following the promising trends of green chemistry. CO_2 is already used as a reagent in relatively few industrial processes such as production of urea, salicylic acid, and some carbonates. Despite limited number of applications of CO_2 in organic synthesis caused mainly by high kinetic inertness and thermodynamic stability of CO_2 [21–24], every year new approaches involving CO_2 have been investigated [25–28]. For many years, carbonylation of aromatic amines by CO_2 was poorly represented in the literature, in contrast to carbonylation of ammonia and aliphatic amines by CO_2 [29–34]. Perhaps, lower nucleophilicity of nitrogen atom in the aromatic ring of aromatic amines decreases their reactivity towards CO_2 [5]. However, in recent years significant progress has been made toward the synthesis of isocyanates, ureas, carbamates, and other compounds using CO_2 and aromatic amines [35–41]. Despite promising results, many of these methods suffer from some limitations such as long reaction times required, harsh reaction conditions, low yields, and other difficulties in application of CO_2 as a carbonylating agent [42,43]. Therefore, some reports are focused on the use of CO_2 as an additive for CO, or as a reaction medium (liquid CO_2) [5,27,44]. Gabriele et al. [44] observed that in carbonylation of amines performed in the presence of CO/air and PdI_2, the addition of CO_2 significantly increased yield of the reaction for aliphatic amines, whereas less satisfactory results were obtained for carbonylation of aromatic amines. Surprisingly, good performance was observed for both aliphatic and aromatic amines when carbonylation was conducted in pure CO_2 as a non-polar aprotic solvent. Using an appropriate amount of CO_2 resulted in nearly three times higher catalytic activity of PdI_2 catalyst [44]. Based on the results obtained by Gabriele, although in many processes it is very difficult to replace CO by CO_2 as carbonylating agent, addition of CO_2 may increase the yield of the carbonylation of amines by CO. Moreover, carbon dioxide is a byproduct formed during industrial production of CO and its complete removal makes an additional complication in the production process. Furthermore, CO_2 exhibits a much stronger suppression effect on the explosion of flammable gases than nitrogen [45], and thus it decreases explosiveness of gases employed in the synthesis (CO and O_2) leading to enhanced safety of the process [46]. Last but not least, presence of CO_2 in a traditional liquid phase under mild pressures (tens of bar) results in generation of a gas-expanded liquid (GXL) phase. GXL retains the beneficial attributes of a conventional solvent (polarity, catalyst/reactant solubility) with some additional advantages: higher miscibility of permanent gases (O_2, CO, etc.) and enhanced transport rates compared to organic solvents at ambient conditions. The enhanced gas solubilities in GXLs may result in reaction rates greater than those achieved in neat organic solvent or supercritical carbon dioxide (sCO_2) [47]. In the case of our process, even if CO_2 cannot serve as a carbonylating agent,

it is interesting to explore other potential benefits of replacing CO with CO_2, i.e., decreasing the amount of CO used and introducing CO_2 without any preconceived notion regarding its exact function.

Inspired by the promising properties of CO_2 and results reported by Gabriele et al. for carbonylation of aniline in the presence of CO_2, K_2PdI_4 as catalyst and without any additives [44], we decided to study the effect of CO_2 as one of the components of $CO/O_2/CO_2$ mixture on the carbonylation of aniline (model aromatic amine) in the presence of our original catalytic system $PdCl_2(X_nPy)_2/Fe/I_2/X_nPy$, at shorter reaction time and under lower total pressure. Also, our goal is to develop our previous catalytic system based on $PdCl_2(X_nPy)_2$ complexes into nanocatalysts, characterized by unique catalytic properties. Based on the results of our recent studies, we turned our attention to derivatives of pyridine as ligands that optimally stabilize palladium NPs [48–51] i.e., the access to the catalyst surface is not restricted, in contrast to bulky ligands [52–54]. Choosing 4-methylpyridine (model derivative of pyridine) as stabilizing ligand allows nanoparticles (NPs) to effectively interact with ligands and the reacting compound(s). In our previous works, we developed a reduction of aromatic nitrocompounds to aromatic amines in the presence of palladium nanoparticles stabilized by 4-methylpyridine (PdNPs/4MePy) [55,56]. Obtained results encourage us investigation of the catalytic activity of PdNPs/4-MePy in another process i.e., oxidative carbonylation of aniline in the presence of mixture $CO_2/CO/O_2$. For the first time, carbonylation of aniline is carried out in the presence of CO_2 and palladium nanoparticles stabilized by 4-methylpyridine.

2. Results and Discussion

Referring to our previous work [56], monodentate N-heterocyclic compounds are potentially a new family of stabilizing agents that could be a starting point for design new catalytically active nanoparticles with higher catalytic efficiency. In this work, the catalytic activity of PdNPs is compared with effectiveness of catalytic system based on Pd(II) complexes in the carbonylation of aniline (AN) to N,N′-diphenylurea (DPU) by $CO_2/CO/O_2$ mixture. Based on our previous results, we proposed the mechanism of AN carbonylation by CO/O_2 in the presence $PdCl_2(X_nPy)_2$ complexes (where: Py = pyridine, X = -Cl or -CH_3, *n* = 0–2), with Pd(II) reduced to Pd(0) in situ in the catalytic cycle, see Scheme 1. Partial precipitation of inactive Pd_{black} reported by Ragaini [57] is one of the proofs of the Pd^0 presence in the system, further supported by our isolation of palladium black precipitated during the reaction of $PdCl_2(PhNH_2)_2$ complex with carbon monoxide [15]. The next step is reoxidation of Pd(0) to Pd(II) and in this cycle both molecular oxygen and iodine are supposed to be potential oxidants responsible for recycling Pd(II) from Pd(0), step 1a–1b. Although oxidation of Pd(0) by oxygen is possible, it is very slow [58]. Alternatively, Pd(0) in 1a may be oxidized during the oxidative addition of I_2 to Pd(0), according to the equation: Pd(0) + $I_2 \rightarrow PdI_2$. Then, HI (instead of water) is released and this HI is oxidized by molecular oxygen: $4HI + O_2 \rightarrow 2I_2 + 2H_2O$ [1]. The intermediate 1b is able to coordinate aniline with subsequent insertion of CO to NH-Pd bond in 1c, creating a new carbon-nitrogen bond, intermediate 1d reductive elimination gives N,N′-diphenylurea, generating Pd(0) species [15]. According to the proposed mechanism presented in Scheme 1, Pd(0) stabilized by pyridine ligands plays a crucial role as an acceptor of oxidizing agent (O_2 or I_2). In order to verify the hypothesis on the participation of Pd(0) in the catalytic cycle, we planned experiments with Pd(0) nanoparticles (PdNPs), and the results (conversion, selectivity, and yield of carbonylation) were compared with the same parameters for process catalyzed by Pd(II) complexes. Prior to that, we searched for the optimal conditions to make both processes, catalyzed by PdNPs and Pd(II) complexes, comparable.

$$X = Me \text{ or } Cl, \, m = 0\text{-}4, \, n = 0\text{-}2, \, Y = Cl \text{ or } I$$
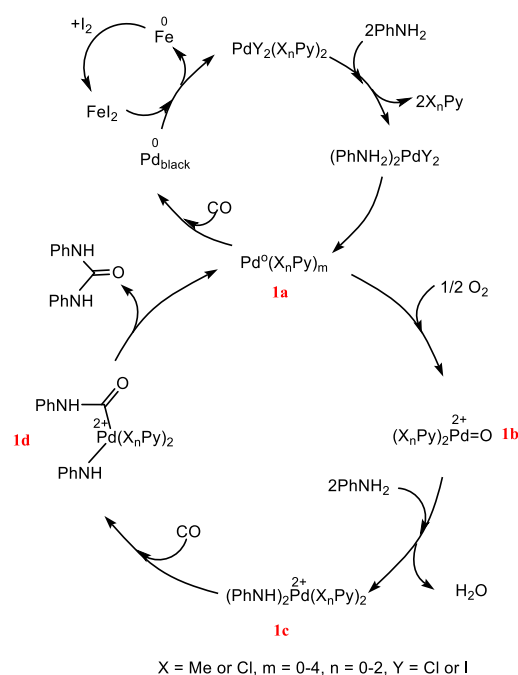
Scheme 1. Proposed path of the carbonylation of aniline by CO/O_2 catalyzed by $PdCl_2(X_nPy)_2$ complexes.

2.1. Optimization of Reaction Conditions of AN Carbonylation with $CO_2/CO/O_2$ Mixture

Conversion of aniline, selectivity towards DPU, and TOF for DPU are presented in Table 1, indicating a strong correlation between the rate of reaction and the amount of CO_2 used. Relatively high conversion and selectivity are observed when no CO_2 is loaded into the system (entry 5, Table 1). However, even a moderate addition of CO_2 is associated with the increasing rate of reaction, and its optimal amount in the gaseous mixture is ca. 50% (entry 4). High yield of DPU (96%) was also observed by Gabriele et al. for carbonylation of aniline performed in the presence of CO_2 and a different Pd-based catalytic system. Authors applied a very simple catalyst (K_2PdI_4), without any co-catalyst and additives; however, a long reaction time (24–72 h) was required [44]. Figure 1 shows that conversion of aniline and selectivity towards DPU decrease drastically when more than 50% of CO_2 is introduced. Eventually, no formation of DPU is observed at 100% fraction of CO_2 (entry 1, Table 1). Investigation of the impact of CO/CO_2 ratio was complemented by additional experiment in which carbonylation of aniline under conditions from entry 4 in Table 1 was conducted in the presence of $Ar/CO/O_2$ instead of $CO_2/CO/O_2$ mixture, and no difference in DPU yield between the two cases was observed. Obtained results suggest that replacing CO with certain amount of CO_2 allows for achieving higher yields of DPU, although, as indicated by the experiment with argon, CO_2 itself does not seem to act as a carbonylating agent. We propose two possible explanations for the beneficial effect of CO_2. First, it is likely that the observed optimal CO/CO_2 ratio is a result of the balance between enhancement of mass transfer by CO_2 (as commonly observed in GXLs) and minimal amount of CO necessary for efficient carbonylation of aniline. In the presence of 88% of CO_2 content, the amount of CO (12%) is lower than required according to stoichiometry, and therefore, unsurprisingly, is associated with lower conversion and TOF values. On the other hand, the presence of CO_2 might prevent (inhibit) possible side reactions, e.g., oxidation of CO to CO_2 (which to some extent may occur in the presence of palladium catalyst). Unless the necessary amount of CO is provided in the system, no DPU is produced and such results confirm that CO_2 is not a source of carbonyl group in this reaction. However, we performed further processes in the presence of CO_2 as an additional gas due to its economic benefits (CO_2 is a natural waste in CO production).

Table 1. Parameters obtained for the carbonylation [a] of aniline with $CO/CO_2/O_2$ mixture, catalyzed by Pd(II) complexes: conversion (C_{AN}), selectivity (S_{DPU}) and turnover frequency (TOF_{DPU}) of the catalyst, depending on the contents of CO_2 in CO_2/CO, iodine, and iron.

Entry	CO_2 in CO/CO_2 [b] (%)	I_2 (mmoL)	Fe (mmoL)	C_{AN} (%)	S_{DPU} [c] (%)	TOF_{DPU} [d]
1 [e]	100	0.12	2.68	12	0	0
2 [e]	88			37	57	202
3 [e]	65			83	83	666
4 [e]	56			84	87	704
5 [e]	0			68	93	608
6	56	0	2.68	10	0	0
7		0	0	10	0	0
8		0.01		46	96	434
9		0.04		71	96	657
10		0.12		73	95	669
11		0.39		69	94	617
12		0.04	0.25	75	96	694
13			0.5	78	98	733
14			1.2	74	96	685
15			2.68	72	95	660
16 [f]			2.68	72	96	667

[a] Reaction conditions unless stated otherwise: $PdCl_2(2,4Cl_2Py)_2$ = 0.056 mmoL, AN = 54 mmoL, ethanol = 20 mL, 3.8 MPa $CO + CO_2$, 0.6 MPa O_2, (100 °C, 60 min, Py = pyridine, AN = aniline, DPU = N,N-diphenylurea. [b] For CO/O_2: (0.6 MPa O_2 and 3.8 MPa CO) the molar ratio $CO:O_2$ = 6:1 ca. For $CO/O_2/CO_2$ (0.6 MPa O_2, 1.7 MPa CO, 2.1 MPa CO_2) the molar ratio $CO:O_2$ = 3:1 ca. [c] Selectivity toward DPU expressed as (mmoL DPU) × (mmoL converted AN)$^{-1}$ [%]. [d] TOF_{DPU} (turnover frequency for AN) = [mmoL of AN reacted selectively to DPU] × [mmoL of Pd(II) complex used]$^{-1}$ × h^{-1}, [e] $PdCl_2Py_2$ used instead of $PdCl_2(2,4Cl_2Py)_2$. [f] 0.6 mL of 2,4-Cl_2Py added.

(A)	(B)
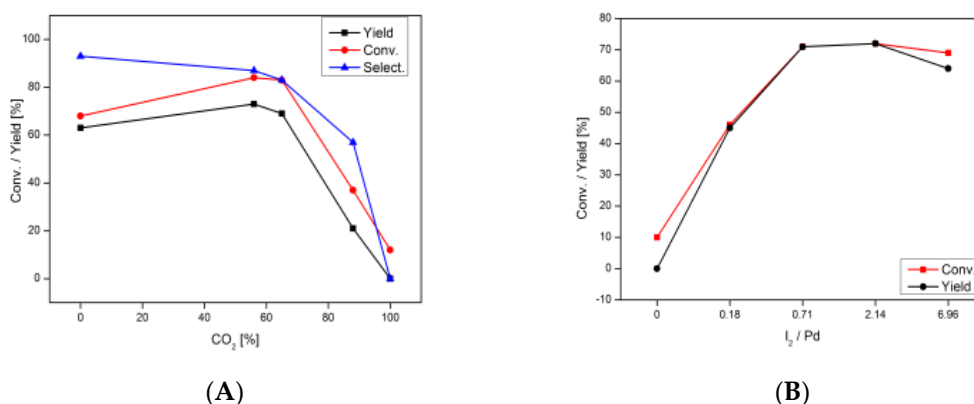
Figure 1. Effect of percentage of CO_2 in CO_2/CO mixture (**A**) and amount of iodine (**B**) on the conversion (Conv.) and yield and selectivity (Select.) of the catalyst. For the reaction conditions see footnotes in Table 1.

The substituent effect in the pyridine ring was investigated for the optimized content of CO_2 in CO_2/CO mixture (i.e., 56%). On the basis of obtained results, there is no consistent trend in the effect of derivatives of pyridine in $PdCl_2$ complexes on the rate of reaction (Figure S1 in Supplementary Material). The slightly higher yield of DPU (comparing to other Pd-based complexes) is noticed for $PdCl_2(2,4-Cl_2Py)_2$ complex, and most further studies in this area are performed in the presence of this complex.

The effect of iodine on the rate of carbonylation was also investigated. As shown in Table 1, when no iodine is used, the desired reaction does not proceed, regardless of the amount of iron present in the system (entries 6–7, Table 1). Increasing amount of iodine results in higher conversion, selectivity and TOF values, with the maximum at 0.04–0.12 mmoL of I_2 (entry 9 and 10, Table 1). This observation, in agreement with previous reports [1,59–62], indicates that iodine might play various crucial roles such

as: (i) recovery of the catalytic system, perhaps by oxidation of iron powder to iron(II), (ii) generation of palladium complexes $[Pd(CO)_3I]^-$, considered to be the catalytically active species, (iii) reoxidation of Pd(0) to Pd(II). However, if a large excess of iodine is used, the yield of DPU decreases, and the TOF value decreases (entry 11, Table 1). This effect may be attributed to undesirable side reactions, such as formation of insoluble anilinium iodide, which limits the amount of free aniline in the system [60,63]. Moreover, excess of iodide ions may get coordinated to Pd(II), effectively competing with other reagents, which is commonly referred to as catalyst poisoning [10,60,64].

The effect of iron on the rate of reaction is minor (entries 12–16, Table 1). Although a small addition of iron to the mixture seems to increase the conversion of aniline and selectivity towards DPU (see entries 12 and 13, Table 1), it is not a significant change. As more iron is introduced to the system, conversion of aniline decreases slightly (entry 14, Table 1). These observations indicate that a certain amount of iron is beneficial and it slightly increases TOF values during DPU formation. In agreement with our report [15], Fe(0) is oxidized by I_2 to Fe(II) and the possible role of Fe(II) is to react with Pd_{black} in order to return Pd_{black} to the catalytic cycle as shown in Scheme 1. In the literature, we can find reports for [1] and against [65] the suggested role of iron. Lower conversion of aniline, when excess of iron is used, can be attributed to the reaction between iron and oxygen, which in turn decreases the amount of necessary oxidizing agent (O_2). Both reactions of metallic iron, with iodine and with O_2, occur easily [66]. Our previous research indicates that even traces of iron (from stainless steel reactor and stirring element) are kinetically significant.

The reaction rate seems to be strongly dependent on the temperature settings selected (see Table 2): at 80 °C the reaction proceeds only to some extent (entry 1). Optimal value for the synthesis of DPU is 100–120 °C (entry 2 and 3) with even higher temperature (140 °C) leading to formation of EPC (entry 4, Table 2, selectivity and TOF values for EPC are placed in parentheses). These results suggest that, after achieving the activation parameters suitable for the formation of DPU, further increase of temperature does not enhance the catalyst activity and may even have a slightly negative impact on the conversion of aniline, possibly due to occurrence of side reactions such as formation of N-ethylaniline, 2-methylquinoline, polyaniline, and EPC (entry 4, Table 2). Further studies were conducted at 100 °C because one of our aims was to operate at desirable energy-saving conditions, i.e., at the lowest temperature allowing formation of satisfactory amount of DPU. The temperature of 100 °C was also chosen for other practical reasons—it was the most appropriate temperature for comparative tests (high conversion and selectivity of Pd(II) complex were observed at this temperature during our previous studies reported in [15]). Although NPs might be more active at 120 °C than at 100 °C, the goal of this work was not to achieve the highest possible activity of catalyst but to study and compare activity of various types of pre-catalysts at the same temperature.

Table 2. Parameters obtained for the carbonylation of aniline by $CO/CO_2/O_2$ catalyzed by $PdCl_2(2,4\text{-}Cl_2Py)_2$: conversion ($C_{AN}$), selectivity ($S_{DPU}$) and turnover frequency (TOF_{DPU}), depending on the temperature [a].

Entry	T (°C)	C_{AN} (%)	S_{DPU} [b] (%)	TOF_{DPU} [c]
1	80	17	98	161
2	100	71	98	671
3	120	86	95	791
4	140	80	71 (20) [d]	550 (154) [e]

[a] Reaction conditions unless stated otherwise: $PdCl_2(2,4Cl_2Py)_2$ = 0.056 mmoL, I_2 = 0.04 mmoL, AN = 54 mmoL, ethanol = 20 mL, 3.8 MPa CO + CO_2, 0.6 MPa O_2, 100 °C, 60 min, Py = pyridine, AN = aniline, DPU = N,N-diphenylurea. [b] Selectivity toward DPU expressed as (mmoL DPU) × (mmoL converted AN)$^{-1}$ [%]. [c] TOF_{DPU} (turnover frequency for AN) = [mmoL of AN reacted selectively to DPU] × [mmoL of $PdCl_2(2,4ClPy)_2$]$^{-1}$ × h^{-1}. [d] Selectivity toward EPC (ethyl N-phenylcarbamate), [e] TOF_{EPC} = (mmoL of EPC formed)(mmoL of $PdCl_2(2,4\text{-}Cl_2Py)$ used)$^{-1}$h^{-1}.

2.2. Synthesis of PdNPs

PdNPs stabilized by 4MePy were synthesized in water, following the procedure [43,50]. Before NPs are used as catalysts they are dried because the presence of excess H_2O in the reaction mixture might diminish the yield of diphenylurea formed during the carbonylation of aniline by CO/O_2 (partial hydrolysis of urea may occur at high temperature) [1]. The TEM images presented in Figure 2 indicate agglomeration after drying (left panel versus middle panel), therefore, we also decided to synthesize NPs in ethanol. Right panel in Figure 2 demonstrates that palladium nanoparticles are not stable in ethanol and bigger aggregates are formed. A more appropriate name for these aggregates would be a palladium-based nanostructural material (PdNM) rather than nanoparticles.

(A)　　　　　　　　　　**(B)**　　　　　　　　　　**(C)**
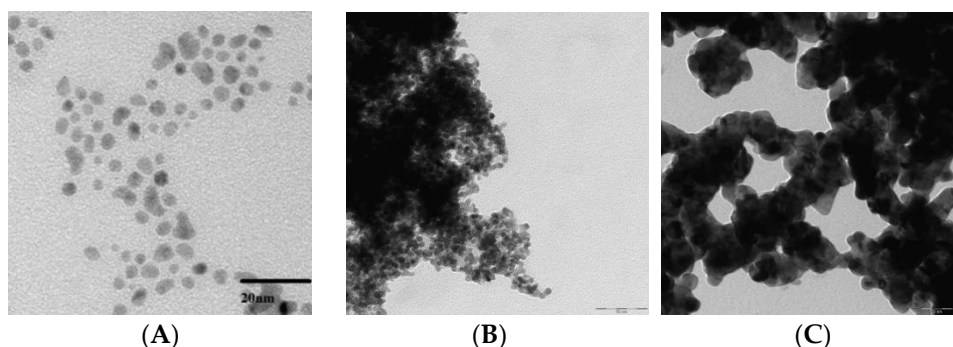
Figure 2. (**A**) TEM image of the PdNPs stabilized by 4-methylpyridine (PdNPs/4MePy) from raw aqueous solution [51]. Pd: $NaBH_4$ molar ratio = 1:2, concentration of $NaBH_4$ solution = 1%. For synthesis conditions see Experimental Section. (**B**) TEM image of the PdNPs stabilized by 4-methylpyridine (PdNPs/4MePy) dried and re-suspended in distilled-deionized water. (**C**) TEM image of the PdNM (palladium-based nanostructural material) stabilized by 4-methylpyridine (PdNM/4MePy) obtained in ethanol.

2.3. Catalytic Activity of NPs Compared with Other Pd Species

Conversion of aniline, selectivity towards DPU, and TOF for DPU formed in the presence of PdNPs/4MePy are presented in Table 3. Results obtained for PdNPs are compared with results obtained for commercially available Pd_{black} and two Pd(II) complexes: with 4MePy (the ligand that forms the most stable PdNPs) and with 2,4-Cl_2Py (the ligand forming the most catalytically active complex of Pd(II)). TOF values of PdNPs, Pd_{black}, and Pd(II) complex, measured after 60 min demonstrate that all studied substances are effective pre-catalysts for carbonylation of aniline during the standard time of reaction. The highest yield observed for PdNPs indicates that PdNPs are either catalytically active species or the most efficient source of other catalytically active species e.g., $[Pd(CO)_3I]^-$ [10]. Perhaps, when Pd(II) complex is applied as a pre-catalyst, it takes longer time to generate in situ catalytically active Pd(0) species from Pd(II), which might explain TOF for Pd(II) complexes being lower than for PdNPs. Our hypothesis, that active species responsible for catalytic activity are easily formed from PdNPs, is confirmed by results obtained for initial stages of the process (i.e., reaction carried out within first 15 min)-significant difference between TOF of PdNPs and TOF of Pd(II) complex is noticed. It is possible that, when carbonylation is carried out in the presence of PdNPs, catalytically active Pd(0) species are immediately present in the reaction from the beginning of the process. Differences in TOF values noticed for Pd(0) in the form of Pd_{black} (entry 4) and Pd(0) in the form of PdNM (entry 3) indicate that higher catalytic activity of PdNM might have an origin in the nanostructure of investigated material (image in the right panel of Figure 2 displays the PdNM formed from PdNPs with diameter ca. 10 nm). The lowest TOF value observed for Pd_{black} suggests that catalytically active species are not in the form of a heterogeneous bulk metal, but rather homogeneous complexes (with Pd^0), as suggested in the literature [60]. Such a hypothesis that homogeneous complexes (with Pd^0) are the real catalysts

can explain why TOF for Pd(II) is higher than for Pd(0) –formation of homogeneous Pd(0) species from bulky Pd_{black} is more difficult than from Pd(II).

Table 3. Parameters obtained for the carbonylation of aniline by $CO/CO_2/O_2$: conversion (C_{AN}), selectivity (S_{DPU}) and turnover frequency (TOF_{DPU}), depending on the catalyst [a].

Entry	Catalyst	C_{AN} (%)	S_{DPU} [b] (%)	TOF_{DPU} [c]
1	PdNPs/4MePy	92	88	781
2 [d]	PdNPs/4MePy	27	89	926
3	PdNM/4MePy [e]	80	84	646
4	Pd_{black}	60	89	515
5	Pd_{black} [f]	72	89	617
6	$PdCl_2(4MePy)_2$	83	87	656
7 [d]	$PdCl_2(2,4Cl_2Py)_2$	16	88	540

Reaction conditions unless stated otherwise: Pd-based catalyst/Fe/I_2 = 0.056/0.5/0.12 mmoL, AN = 54 mmoL, 1.5 MPa CO, 1.9 MPa CO_2, 0.6 MPa O_2, 20 mL EtOH, 60 min. Py = pyridine, AN = aniline, DPU = N,N-diphenylurea. [b] Selectivity toward DPU expressed as (mmoL DPU) × (mmoL converted AN)$^{-1}$ [%]. [c] TOF_{DPU} (turnover frequency for AN) = [mmoL of AN reacted selectively to DPU] × [mmoL of Pd(II) complex used]$^{-1}$ × h^{-1}. [d] 15 min. [e] PdNM = palladium-based nanostructural material was prepared in ethanol instead of water and raw solution of PdNM was introduced to the reactor (the volume of the solution was adjusted to obtain 0.056 mmoL of Pd). [f] 66 μL of 4MePy added.

3. Materials and Methods

3.1. Materials

Palladium chloride, sodium chloride, and sodium borohydride were used as received. Pyridine (Py), 2-methylpyridine (2-MePy), 3-methylpyridine (3-MePy), 4-methylpyridine (4-MePy), 2,6-dimethylpyridine (2,6-Me_2Py), 2,4-dimethylpyridine (2,4-Me_2Py), 3,5-dimethylpyridine (3,5-Me_2Py), 2-chloropyridine (2-ClPy), 3-chloropyridine (3-ClPy), 2,4-dichloropyridine (2,4-Cl_2Py), aniline, and ethanol were distilled (or fractionally distilled) over drying agent and stored under argon. 2,6-dichloropyridine (2,6-Cl_2Py), 3,5-dichloropyridine (3,5-Cl_2Py), iron powder, and iodine were used as received. Ultrapure (Milli-Q, 18.2 MΩ·cm resistivity at 25 °C) water was used in all experiments.

3.2. Synthesis of Palladium Nanoparticles

PdNPs were prepared according to the method described elsewhere [48,55]. NaCl (0.188 mmoL; 0.11 g) and $PdCl_2$ (0.084 mmoL; 0.015 g) were dissolved in 6 mL of ultrapure water and stirred at room temperature to form water soluble $PdCl_4^{2-}$ species. Then, a freshly prepared solution of ligand (derivative of pyridine; 0.628 mmoL in 9 mL of water) was added, stirred for 20 min, and reduced by $NaBH_4$ (1% w/v, 1.1 mL) added in 20 μL portions. The progress of reaction was observed as an immediate darkening of the mixture from light orange to dark brown (almost black). The resulting PdNPs were stirred for 30 min. In some experiments, for comparison purposes, nanoparticles were synthesized in ethanol instead of water. The size of centrifuged NPs as well as centrifuged and dried NPs was measured by transmission electron microscopy (TEM). The composition of Pd/ligand expressed as a percentage of the organic ligand and the metal in the centrifuged and dried palladium nanoparticles stabilized by 4-methylpyridine (PdNPs/4MePy) was determined by thermogravimetry (TG) under nitrogen atmosphere, with the heating rate = 10 K/min (see Figure S1 in Supplementary Information).

3.3. Techniques

Transmission electron microscopy (TEM) observations were carried out using JEM 1400 JEOL Co. microscope, at 120 kV acceleration voltage. The samples were obtained by casting aqueous (or ethanol) solution of palladium nanoparticles onto a carbon coated nickel microgrid (200 mesh) and air-dried overnight. The thermogravimetric (TG) measurements of PdNPs/4-MePy were performed

with thermogravimeter Q50-1261 TA Instruments (USA) under nitrogen flow (6 dm^3/h), heating rate = 10 K/min. Weight loss during thermal decomposition of PdNPs/4-MePy was determined in the temperature range 40–600 °C. TG measurements were performed in platinum pan, and the weight of the sample was around 1–2 mg. Results presented in this paper are the arithmetic mean of three repetitions, and the difference of results in a series of determinations of the sample was up to 2%.

3.4. Carbonylation of Aniline by $CO/CO_2/O_2$ to N,N′-Diphenylurea

The procedure described elsewhere [15] was applied with some modifications. Briefly, the reaction was carried out in a 200 mL stainless-steel autoclave equipped with magnetic stirrer. Before the experiment, the autoclave was heated at 120 °C for 3 h (evaporation of water in order to avoid shifting the balance to the left, which may occur in the presence of an excess of water at high temperature) and cooled down to room temperature. Subsequently, one of the following catalysts: $PdCl_2(X_nPy)_2$, $PdCl_2$, Pd_{black}, or PdNPs (0.056 mmoL), and Fe powder (0–2.7 mmoL) were placed in the autoclave, the air was evacuated, and the system was filled with purified argon. Then, under a gentle stream of argon, other reagents and solvents were added: I_2 (0–0.39 mmoL), aniline (54 mmoL), ethanol (20 mL), and optionally Py or X_nPy (6.2 mmoL). After getting its cover closed, the autoclave was directly filled with molecular oxygen (0.6 MPa), a mixture of carbon dioxide and carbon monoxide (pressure of CO_2/CO = 3.4 MPa), then placed in a hot oil bath, and kept at 80–140 °C for 15 or 60 min, depending on the reaction. After 15 or 60 min (depending on the reaction), the autoclave was cooled in a water bath, and then vented. The solid phase obtained after centrifugation (15,000 rpm for 15 min) in the form of white needles (with traces of precipitated palladium black) was re-crystallized from methanol and analyzed by elemental analysis, IR and ^{1}H NMR. N,N-diphenylurea was identified on the basis of elemental analysis % (exp./calc.): C(73.60/73.57), H (5.75/5.70), N (13,22/13.20); FT-IR (KBr): 3326, 3283(s) ν_{NH}; 3000–3100 (s) $\nu_{C\text{-}H\ aromat}$; 1648 (s) $\nu_{C=O}$; 1595, 1555 (m) $\nu_{C=Caromat}$; 1496, 1444 (m) $\nu_{N\text{-}H}$; 1313, 1233 (m) $\nu_{C\text{-}N}$; 755, 697 (s) $\nu_{C\text{-}Haromat}$ cm^{-1}. M.P. = 235–237 °C; ^{1}H NMR (300 MHz, DMSO): δ (ppm): 8.65 (s, 2 H), 7.46 (d, 4 H), 7.28 (t, 4 H), 6.97 (t, 2 H), and obtained values are in agreement with literature data [67]. Analysis of the liquid phase was performed using gas chromatography (GC-FID, GC-MS). Calculation of conversion of aniline was based on GC-FID analysis with n-decyl alcohol as standard.

4. Conclusions

In this work, the effect of CO_2 on the rate of carbonylation of aniline to N,N′-diphenylurea was investigated. Taking into account results obtained for various types of Pd-based pre-catalysts—namely, PdNPs, PdNM, Pd(0) and Pd(II) complexes—the highest TOF is observed for PdNPs. Thus, we suggest that PdNPs act as active species or as the most efficient source of other catalytically active Pd(0) species. High yields observed for Pd(II) complexes support proposed mechanism where Pd(II) is easily reduced to catalytically active Pd(0) during catalytic cycle. We conclude that introduction of PdNPs to the reaction mixture instead of Pd_{black} or Pd(II) results in higher conversion and turnover frequency. We believe that obtained results may be helpful in elucidating the role of metallic nanoparticles in other organic processes.

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