



Oxidative carbonylation of phenols catalyzed by homogeneous and heterogeneous Pd precursors

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ABSTRACT

Homogeneous and heterogeneous Pd-based catalysts (in the presence of Co(acac)₃/ligand/BQ/TBAB and molecular sieve 4A), have been compared in the oxidative carbonylation of phenols. The best yields have been observed in the presence of bulky bidentate N-N ligands such as dmphen and triind. The comparison between homogeneous and heterogeneous systems shows similar behavior in terms of yield and selectivity in DPC, as in 4 h of reaction only small differences of activity have been observed. On the contrary, in 20 h of reaction only the systems Pd(OAc)₂/Co(acac)₃/dmphen/BQ/TBAB and Pd(OAc)₂/Co(acac)₃/triind/BQ/TBAB double the yield in DPC, while with the other systems the conversion is blocked. The beneficial effect of the ligands and of TBAB might be due to their capacity of inhibiting the growing of Pd nanoparticles that are likely to form, thus easing their reoxidation to Pd(II) species. The initial rate of phenol or methyl substituted phenols in CH₂Cl₂ as a solvent are only slightly influenced, except in the case of bulkier 2,6-dimethylphenol. The conversion vs. time profile evidences that fast catalyst deactivation occurs in any case.

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1. Introduction

Market growth for aromatic polycarbonates (PCs) is higher than 10%/year from the late 1990s. Currently, the worldwide production capacity of PC is about 2 million t/year, and the construction of new PC plants is in progress. Nowadays, PC is produced mostly via phosgene processes, which are based on interfacial step polymerization of bisphenol A (BPA) and COCl₂. The major drawbacks of these processes are of environmental and safety nature due to the highly toxic, aggressive and corrosive properties of COCl₂, the large amounts of CH₂Cl₂ as the solvent (ca. 10 times the weight of the final products) and to the co-production of NaCl [1]. Recently several researches have been focused on COCl₂-free alternative routes to PC by transesterification process using diphenyl carbonate (DPC) in place of COCl₂ [2].

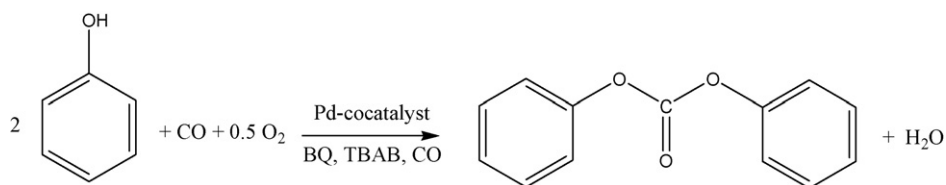
A promising route to DPC is the oxidative carbonylation of phenol catalyzed by Pd-based systems [2–21] (Scheme 1).

It has been reported that Pd(OAc)₂, in phenol as a solvent at 50 °C, is readily reduced to Pd(I), Pd(0) complexes or to Pd metal giant clusters by CO to give CO₂ and phenyl acetate and that, when the reaction is carried out in the presence of O₂, formation of DPC is observed [6,7]. Reoxidation of such a reduced Pd species to Pd(II)

turns the system into a catalytic one, however, direct reoxidation with oxygen is slow, if palladium black is formed. Further improvement of the process is a multistep electron transfer system, which speeds up the oxidation stage [8] by using benzoquinone (BQ) and a redox couple based on salts of Mn, Co, Ce or Cu [9,11–15] in the presence of tetrabutylammonium bromide (TBAB), which is known to act both as stabilizing agent for Pd(II) and Pd(0) as well as surfactant agent for Pd metal nanostructure, thus limiting its aggregation [8,10,22–25]. In this field much work has been recently carried out by several authors on studying the role of Pd nanoparticles and soluble leached moiety in Suzuki and Heck reactions, thus suggesting the reactions occur in homogeneous phase [26–29].

The oxidative carbonylation of phenol catalyzed by heterogeneous Pd-based systems has been widely reported [14–18]. However, due to the necessity of using homogeneous promoters such as BQ and TBAB, and the fact that Pd is likely to undergo a redox process, the nature of the active species as well as the phase where the reaction takes place are not clear. The increase of the Pd particles average diameter as well as the formation of surface bimetallic moiety suggest that surface reconstruction and particles sintering are strictly related with catalyst poisoning, which in turn is, connected with the homogeneous catalyst deactivation [30–32]. This paper deals with the comparison of homogeneous with heterogeneous Pd catalyst precursors for the oxidative carbonylation of phenols in the presence of ammonium halides and [Co(acac)₃].

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Scheme 1. Oxidative carbonylation of phenol.

2. Experimental

2.1. Materials

Carbon monoxide and oxygen (purity higher than 99%) were supplied by SIAD Spa (Italy), phenol 99%, biochemical grade, tetrabutylammonium bromide (TBAB) 99% and 1,4-benzoquinone (BQ) 99% were purchased from Acros Chemicals. Pd(OAc)₂ 98%, PdCl₂ 99%, Co(acac)₃ 98%, Co(acac)₂ 99%, 2,9-methyl-1,10-phenantroline (dmphen), indole (ind) 99% were purchased from Aldrich Chemicals. 1,3-bis(diphenylphosphino)propane (dppp), 1,2-bis(diphenylphosphino)ethane (dppe), bis(diphenylphosphino)methane (dppm), triphenylphosphine (tpp) and 1,1'-bis(diphenylphosphino)ferrocene (dppf) were purchased from Aldrich Chemicals.

The indole dimer hydrochloride (3-(indolin-2-yl)indole) hydrochloride, diind and trimer sulfate (3,3'-(2-aminophenethylidene)di-indole sulfate, triind) were prepared according to [33,34].

The complexes were synthesized following procedures reported in literature: [PdCl₂(dppm)], [PdCl₂(dppe)], [PdCl₂(dppp)] and [PdCl₂(dppb)] [35]; [PdCl₂(tpp)₂] and [Pd(OAc)₂(tpp)₂] [36], [Pd(OAc)₂(dppb)] [37], [Pd(OAc)₂(dppf)] and [PdCl₂(dppf)] [38], [Pd(CO)(tpp)₃] [39].

Amberlyst 15 and Amberlyst 36 (trade mark of Rohm and Haas) are macroreticular sulfonated styrene-divinylbenzene resins (surface area 36 and 32 m² g⁻¹ respectively) were purchased from Aldrich. γ-Al₂O₃ (surface area 210 m² g⁻¹) were purchased from Condea.

Pd/C catalysts are commercial Engelhard catalysts Escat 11 (5 wt.% Pd) and Escat 18 (0.5 wt.% Pd), Pd/Al₂O₃ (1 wt.% Pd) were prepared by ionic exchange of K₂PdCl₄ at pH 7 with γ-Al₂O₃ following the conventional procedure [40]. Pd/Amberlyst 15 and Pd/Amberlyst 36 catalysts were also prepared by ion exchange of [Pd(NH₃)₄]Cl₂ [40]. Pd/polyketone was prepared by impregnation of Pd(OAc)₂ into polyketone [40], the latter prepared by copolymerization of CO and ethene [41].

Amberlyst 15 was exchanged with tetrabutylammonium cations in an aqueous solution of TBAB under agitation for 20 h (1 g of resins in 100 ml of solution 1 mol l⁻¹).

2.2. Experimental setup

The experiments were carried out in two PTFE lined stainless steel autoclaves of ca. 70 ml and 250 ml of capacity, both provided with magnetic stirrer, temperature control and gas phase sampler. Most of the experiments were repeated in an autoclave in which the reagents and catalyst were contained in a glass beaker and the same results were found. The 250 ml autoclave, used for the kinetic studies, was also equipped with a capillary of 0.2 mm for sampling the liquid phase (Fig. 1).

2.3. Experimental procedure

When using the 70 ml autoclave, typical reaction condition were: $T=378\text{ K}$, $P=6\text{ MPa}$ $\text{CO/O}_2=10/1$ molar ratio, phe-

nols 80 mmol which act also as solvent, Pd(OAc)₂=0.01 mmol, Pd(OAc)₂/BQ/Co(acac)₃/dmphen 1/30/8/5 molar ratio, reaction time 1–5 h. In TBAB Pd/TBAB=1/60 molar ratio was added, as well as molecular sieve 4A (2 g) as water scavenger. Then the autoclave was pressurized with the mixture of carbon monoxide and oxygen. After a given time, typically 1–20 h, the autoclave was cooled to room temperature and vented. Products were analyzed by an Agilent 6890 GC instrument equipped with a 30 m 300 μm HP5 column. CO and CO₂ in the gas phase were analyzed by GC, using an 18 ft=1/8" SS Silica Gel, 60/80 packed column.

Kinetic measurements were carried out employing dichloromethane as a solvent and sampling the organic phase through the capillary. During the sampling the agitation was interrupted in order to stop the reaction. In a typical experiment 80 mmol of phenol was charged into a beaker, placed in the autoclave together with 5.88 mmol of diphenyl ether as internal standard, and the catalytic system dissolved in 100 ml of CH₂Cl₂ (typically Pd(OAc)₂ 0.04 mmol, Pd(OAc)₂/BQ/Co(acac)₃/dmphen/TBAB 1/30/8/5/60 molar ratio). Molecular sieve 4A (3–4 g) were placed into a stainless steel basket hanged over the magnetic stirrer (Fig. 1). The use of the basket avoids the problems of agitation and at the same time ensures efficient exchanging solution-molecular sieve; in addition, it allows a simpler sampling procedures of the liquid phase, and avoid the problems connected with the presence of dust which may stack capillary and valve. Minimal corrosion of the stainless steel basket does not influence the reaction rate because no difference of activity has been observed when molecular sieve is used suspended into the reaction solution.

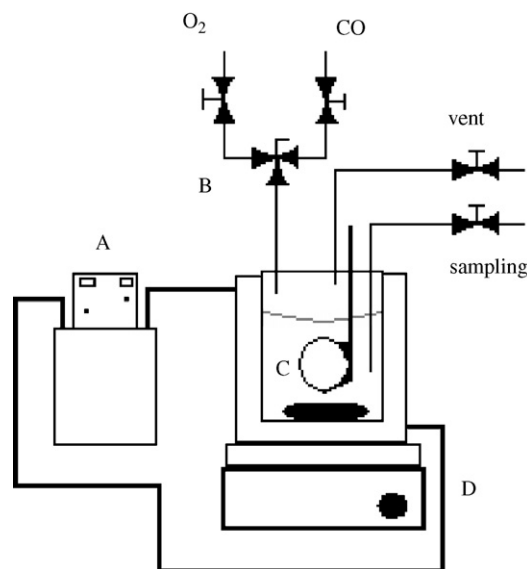


Fig. 1. Reaction system employed in the kinetic runs: A, thermostat; B, gas manifold; C, thermocouple housing and basket holder; D, magnetic stirrer driver.

3. Results and discussion

3.1. Activity and selectivity of different catalytic systems in solvent-free conditions

In the previous papers the multistep catalytic system in the oxidative carbonylation of phenol (Scheme 1) were optimized: for instance, at $T=373\text{ K}$, $P=60\text{ bar}$, $\text{O}_2/\text{CO}=1/10$, phenol 80 mmol in solvent-free conditions, by using the system $\text{Pd}(\text{OAc})_2/\text{dmphen}/\text{Co}(\text{acac})_3/\text{BQ}/\text{TBAB}=1/5/8/30/60$ a TON of 360 after 2 h was found [9,10]. The main side reactions were the oxidation of CO to CO_2 , the formation of phenyl salicylate and biphenyls.

In the present paper, in preliminary experiments, we used this system also in the presence of molecular sieve 4A. The activity is not significantly affected (Table 1 entry 19), but a neat improvement of the reproducibility of the experiments is observed.

Under these experimental conditions, the comparison of different catalytic systems is reported in Tables 1 and 2.

In 4 h of reaction the presence of added ligands and/or different Pd complex do not increase the productivity of the catalytic system $\text{Pd}^*/\text{dmphen}/\text{Co}(\text{acac})_3/\text{BQ}/\text{TBAB}$ significantly. The low yield in DPC attained by using $[\text{PdBr}_4(\text{NBu}_4)_2]$ (Tables 1 and 2, entry 3) or the poor results obtained using the preformed catalytic system (Table 1 entries 15, 20 and Table 2 entries 15, 20–22), suggest that the active catalytic species is also related to the presence of phenol and BQ in the reaction environment.

In 20 h of reaction, however, the catalytic systems containing dmphen and triind (Table 2 entries 19 and 25) double the yield with respect to PdCl_2 and $\text{Pd}(\text{OAc})_2$ (Table 2 entries 1 and 2). The

reasons of such a behavior are not clear, however, a stabilization action of the nitrogen ligands on the catalytic intermediates can be conjectured.

$\text{Pd}(\text{II})$ -phosphines complexes show poor catalytic activity (Tables 1 and 2 entries 4–12), except $[\text{PdX}_2(\text{dppf})]$ ($X=\text{OAc}$ and Cl ; Tables 1 and 2 entries 9, 12), which reach conversions and TONs comparable with those attained by the most active systems. Quite interesting, also by using $[\text{PdX}_2(\text{tpp})_2]$ complexes ($X=\text{OAc}$ and Cl ; Tables 1 and 2 entries 8, 11), yields in DPC are comparable or even higher than those obtained with other chelating phosphine complexes. Similar results are obtained by using complex such as $[\text{Pd}(\text{CO})(\text{tpp})_3]$ (Tables 1 and 2 entry 13), according to the accepted reaction mechanism which involves the $\text{P}(\text{II}) \rightarrow \text{Pd}(\text{0})$ reduction and the $\text{P}(\text{0}) \rightarrow \text{Pd}(\text{II})$ reoxidation steps [9–14].

In all cases after 4 h the conversion toward DPC is practically blocked, except in those experiments carried out in the presence of dmphen and triind ligands. Although, both ligands allow an increase of the final yield in DPC their role in the mechanism is not clear. They may react with the metals (Pd and Co) to form complexes which can be more active. For instance, it is likely that dmphen forms well known $\text{Pd}(\text{II})$ complex whose reactivity in the oxidative carbonylation have been previously tested [20], while $\text{Pd}(\text{II})$ -triind complexes have not yet been characterized.

The activity and the selectivity of the supported Pd catalysts (Table 1 entries 24–28), after 4 h of reaction, are similar to those obtained with the best catalytic homogeneous systems (except Pd/polyketone Table 1 entry 28). In 20 h of reaction (Table 2 entries 27–31) the yield in DPC does not change thus indicating a catalyst deactivation.

Table 1

Activity of different Pd catalyst precursors on yield and selectivity to DPC after 4 h of reaction. Run conditions: T , 378 K; P , 60 bar; $\text{O}_2/\text{CO}=1/10$; molecular sieve 4A 2 g; $\text{Pd}^*/\text{Co}(\text{acac})_3/\text{BQ}/\text{TBAB}=1/8/30/60$; phenol 80 mmol acting also as a solvent.

Entry	Pd^*	DPC selectivity [%]	DPC yield [%]	TON	TOF [h^{-1}]
1	PdCl_2	91	5.0	450	112
2	$\text{Pd}(\text{OAc})_2$	91	4.9	440	110
3	$[\text{PdBr}_4(\text{NBu}_4)_2]$	88	2.9	261	65
4	$[\text{PdCl}_2(\text{dppb})]$	90	2.7	245	61
5	$[\text{PdCl}_2(\text{dppp})]$	87	1.3	114	29
6	$[\text{PdCl}_2(\text{dppe})]$	60	0.10	9.1	2.3
7	$[\text{PdCl}_2(\text{dppm})]$	89	2.3	203	51
8	$[\text{PdCl}_2(\text{tpp})_2]$	90	4.1	397	99
9	$[\text{PdCl}_2(\text{dppf})]$	92	4.2	380	95
10	$[\text{Pd}(\text{OAc})_2(\text{dppb})]$	88	3.1	280	70
11	$[\text{Pd}(\text{OAc})_2(\text{tpp})_2]$	87	2.3	203	51
12	$[\text{Pd}(\text{OAc})_2(\text{dppf})]$	90	4.1	370	92
13	$[\text{Pd}(\text{CO})(\text{tpp})_3]$	90	4.2	380	95
14	$\text{PdCl}_2-(\text{dmphen})^a$	89	6.1	550	137
15	$\text{PdCl}_2-(\text{dmphen})\text{PF}^{a,b}$	82	2.4	204	51
16	$\text{PdCl}_2-(\text{ind})^a$	90	4.0	360	90
17	$\text{PdCl}_2-(\text{diind})^a$	90	2.3	203	51
18	$\text{PdCl}_2-(\text{triind})^a$	94	4.2	380	95
19	$\text{Pd}(\text{OAc})_2-(\text{dmphen})^a$	95	4.9	440	110
20	$\text{Pd}(\text{OAc})_2-(\text{dmphen})\text{PF}^{a,b}$	83	3.2	290	73
21	$\text{Pd}(\text{OAc})_2-(\text{ind})^a$	95	4.2	380	95
22	$\text{Pd}(\text{OAc})_2-(\text{diind})^a$	91	4.0	360	90
23	$\text{Pd}(\text{OAc})_2-(\text{triind})^a$	95	5.0	460	115
24	$\text{Pd}/\text{Al}_2\text{O}_3$ (1%) ^c	92	5.1		
25	$\text{Pd}/\text{Amberlyst 15}$ (5%) ^d	90	5.1		
26	$\text{Pd}/\text{Amberlyst 36}$ (5%) ^d	90	5.1		
27	Pd/C (5%) ^d	94	4.9		
28	$\text{Pd}/\text{polyketone}$ (5%) ^d	45	0.9		

^a $\text{Pd}/\text{ligand}=1/5$.

^b Preformed $[\text{Pd}(\text{dmphen})\text{X}_2]$ complex was prepared as follows: loaded PdX_2 0.01 mmol, TBAB 0.6 mmol, dmphen 0.05 mmol, CH_2Cl_2 5 ml, 5 MPa of $\text{O}_2/\text{CO}=1/10$, heated to 378 K for 10 min, cooled to 298 K and evaporated the solvent in N_2 flow.

^c Loaded 200 mg of catalyst.

^d Loaded 100 mg of catalyst.

Table 2
Activity of different Pd catalyst precursors on yield and selectivity to DPC after 20 h of reaction. Run conditions: T, 378 K; P, 60 bar; O₂/CO = 1/10; molecular sieve 4A 2 g; Pd^a/Co(acac)₃/BQ/TBAB = 1/8/30/60; phenol 80 mmol acting also as a solvent.

Entry	Pd ^a	DPC selectivity [%]	DPC yield [%]	TON	TOF [h ⁻¹]
1	PdCl ₂	92	5.2	460	23
2	Pd(OAc) ₂	92	4.8	420	21
3	[PdBr ₄ (NBu ₄) ₂]	87	2.7	240	12
4	[PdCl ₂ (dppb)]	90	3.3	300	15
5	[PdCl ₂ (dppp)]	87	2.7	240	12
6	[PdCl ₂ (dppe)]	60	0.13	12	0.6
7	[PdCl ₂ (dppm)]	89	3.5	310	15
8	[PdCl ₂ (tpp) ₂]	89	3.6	330	16
9	[PdCl ₂ (dppf)]	90	6.9	650	33
10	[Pd(OAc) ₂ (dppb)]	90	3.3	300	15
11	[Pd(OAc) ₂ (tpp) ₂]	86	3.0	270	14
12	[Pd(OAc) ₂ (dppf)]	90	5.1	450	22
13	[PdCO(tpp) ₃]	88	4.3	369	18
14	PdCl ₂ -(dmphen) ^a	88	6.5	572	29
15	PdCl ₂ -(dmphen)PF ^{a,b}	80	3.2	232	12
16	PdCl ₂ -(ind) ^a	92	5.1	450	22
17	PdCl ₂ -(diind) ^a	86	3.3	300	15
18	PdCl ₂ -(trind) ^a	91	6.0	530	26
19	Pd(OAc) ₂ -(dmphen) ^a	94	11	980	49
20	Pd(OAc) ₂ PF ^b	80	4.0	344	17
21	Pd(OAc) ₂ -(dmphen)PF ^{a,b,c}	80	3.4	302	15
22	Pd(OAc) ₂ -(dmphen)-Co-PF ^{a,b,d}	80	3.4	302	15
23	Pd(OAc) ₂ -(ind) ^a	93	8.1	720	36
24	Pd(OAc) ₂ -(diind) ^a	94	2.1	181	9.0
25	Pd(OAc) ₂ -(trind) ^a	94	11	980	49
26	Pd(OAc) ₂ -(cox) ^a	89	3.6	330	16
27	Pd/Al ₂ O ₃ (1%) ^e	90	4.2		
28	Pd/Amberlyst 15 (5%) ^f	90	5.2		
29	Pd/Amberlyst 36 (5%) ^f	90	5.3		
30	Pd/polyketone	42	1.0		
31	Pd/C (5%) ^f	90	5.2		

^a Pd/ligand = 1/5.

^b Preformed PdX₂ complex was prepared as follows: loaded PdX₂ 0.01 mmol, TBAB 0.6 mmol, CH₂Cl₂ 5 ml, 5 MPa of O₂/CO = 1/10, heated to 378 K for 10 min, cooled at 298 K and evaporated the solvent in N₂ flow.

^c As in (b) plus dmphen 0.05 mmol.

^d As in (c) plus Co(acac)₃ 0.08 mmol.

^e Loaded 200 mg of catalyst.

^f Loaded 100 mg of catalyst.

These findings, according to previously reported results, suggest that the formation of nanoparticles of Pd may be an important step of the catalysis also when homogeneous precursors are used.

In order to verify such a hypothesis the comparison of the activity of different reduced Pd is reported in Table 3. Reduced Pd was prepared by reaction of Pd(OAc)₂ with H₂ in CH₂Cl₂ at 378 K at 20 bar of pressure, in the presence of dmphen and TBAB or in their

Table 3
Activity and selectivity of different Pd metal precursors on yield and selectivity to DPC after 20 h of reaction without solvent. Run conditions: T, 378 K; P, 60 bar; O₂/CO = 1/10; molecular sieve 4A 2 g; Pd(OAc)₂/Co(acac)₃/BQ/TBAB = 1/8/30/60; phenol 80 mmol.

Catalyst	DPC selectivity [%]	DPC yield [%]	TON	TOF [h ⁻¹]
Pd ^a	9	0.1	9	0.45
Pd-dmphen ^b	80	4.0	360	18
Pd-TBAB ^c	78	4.0	360	18
Pd-dmphen-TBAB ^d	80	3.8	340	17

^a Prepared in situ by reduction of 0.01 mmol of Pd(OAc)₂ in CH₂Cl₂, at 378 K, 2 MPa of H₂ for 10 min, the solvent is removed by evaporation under N₂.

^b Prepared as in (a) in the presence of 0.05 mmol of dmphen.

^c Prepared as in (a) in the presence of 0.6 mmol of TBAB.

^d Prepared as in (a) in the presence of 0.05 mmol of dmphen and 0.6 mmol of TBAB.

absence. In the latter case a mirror of metallic Pd forms, which coats the internal wall of the reaction beaker. The oxidative carbonylation of phenol occurs to a significant extent, comparable to when a homogeneous precursor is used, only when the reduction is carried out in the presence of dmphen and TBAB. These results indicate that the above hypothesis is quite reasonable. It is also likely that the ligand and TBAB prevent the growing of colloidal Pd nanoparticles.

3.2. Effect of removal a component at the time from the catalytic system

The effect of removal a component at the time from the catalytic system has been studied using the catalytic system Pd(OAc)₂/Co(acac)₃/dmphen/BQ/TBAB which is the most active. Pd is essential, as in its absence the catalytic activity is insignificant (Table 4). TBAB is a key component. In order to verify the influence of the Br⁻ ion, TBAB was replaced by a sulfonated resin exchanged with the tetrabutylammonium cation. In this case, insignificant yield in DPC with low selectivity is obtained. In addition, the reaction carried out in the presence of LiBr gives negligible yield in DPC. Thus, both ions of TBAB are involved in the catalysis. In the absence of BQ or Co(acac)₃ both yield and selectivity dramatically decrease since reoxidation steps in the catalytic cycle is compromised [10].

Table 4

Effect of removal of a component of the catalytic system of the Pd(OAc)₂-(dmphen) catalyst on yield and selectivity to DPC after 20 h of reaction without solvent. Run conditions: T, 378 K; P, 60 bar; O₂/CO = 1/10; molecular sieve 4A 2 g; phenol 80 mmol; Pd(OAc)₂/Co(acac)₃/dmphen/BQ/TBAB = 1/8/5/30/60.

Component removed	DPC selectivity [%]	DPC yield [%]	TON	TOF [h ⁻¹]
Pd	55	0.1	1 ^a	0.05
O ₂ ^b	45	0.35	31	1.55
BQ	85	1.1	96	4.8
TBAB	45	0.12	10	0.5
TBAB ^c	50	0.16	13	0.65
TBAB ^d	68	0.28	24	1.2
Co ^e	91	5.9	521	26
Co	75	0.80	9	0.45
CO ^f	/	/	/	/

^a Referred to cobalt.

^b BQ as oxidant.

^c Exchanged with a sulfonated resin.

^d LiBr in place of TBAB.

^e Co(acac)₂ in place of Co(acac)₃.

^f CO substituted with CO₂.

On the contrary, the presence of Co(acac)₂ allow lower but significant yield in DPC compared with those obtained with Co(acac)₃, thus suggesting that the oxidation Co(II) → Co(III) is an active step in the reaction mechanism.

The substitution of carbon monoxide with carbon dioxide does not give any reactions, under the conditions investigated, suggesting the formation of phenyl salicylates is a parallel side reaction occurring directly in a intermediate step of the catalytic process and not by electrophile attack of the CO₂ co-produced as side reaction. Furthermore, on loading 2 bar of CO₂ together with CO and O₂ does not significantly modify the reactivity of the system [4].

3.3. Oxidative carbonylation of methyl substituted phenols

It has been found that substituted 1,9-phenanthroline and 2,2'-dipyridyl-Pd complexes are more active and selective as catalyst compared to the unsubstituted ones, because steric hindrance on the neighbors of the metal center favours the reductive elimination product-forming step [16,20].

We checked the role of the steric hindrance by using phenols with different substituents on the aromatic ring (Table 5). It appears that the yield is comparable and that the selectivity is significantly affected when cresols are used. In such cases, the side products are complex mixtures of ring substitution, methyl oxidation and condensation. Thus, the methyl group favours the side reactions more than the formation of DPC, which is little effected.

The oxidative carbonylation of CH₃-substituted phenols has been studied also in CH₂Cl₂. The results are reported in Table 6. The observed decreasing of TON might be due to the fact that phenols are diluted in the solvent. The selectivity is slightly higher than that observed in solvent-less conditions. It is noteworthy that 2,6-dimethylphenol is more reactive than phenol and cresols, which cannot be simply ascribed to the inductive effect of the

Table 5

Reactivity of substituted methylphenols on yield and selectivity to diarylcarbonate after 4 h of reaction without solvent in the presence of the catalytic system Pd(OAc)₂-(dmphen). Run conditions: T, 378 K; P, 60 bar; O₂/CO = 1/10; molecular sieve 4A 2 g; Pd(OAc)₂/Co(acac)₃/dmphen/BQ/TBAB = 1/8/5/30/60; phenols 80 mmol.

Substrate	Carbonate selectivity [%]	Carbonate yield [%]	TON	TOF [h ⁻¹]
Phenol	95	4.9	440	110
o-cresol	61	5.1	463	116
m-cresol	85	4.8	440	110
p-cresol	60	5.2	470	118

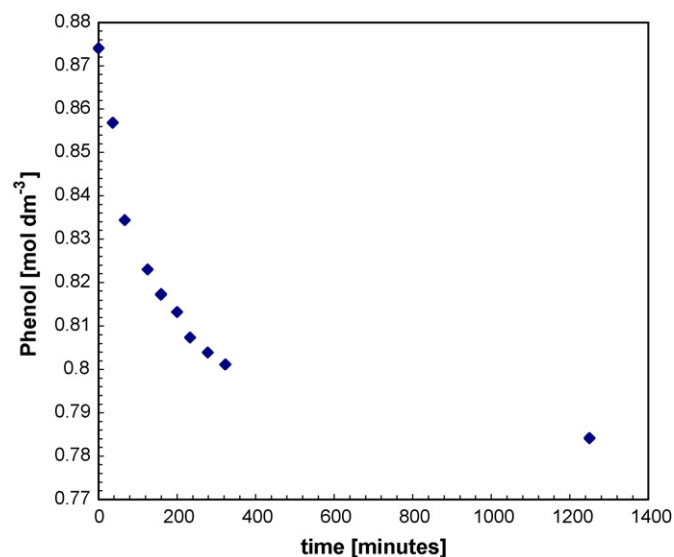


Fig. 2. Phenol consumption profile. Run conditions: T, 382 K; P, 60 bar; O₂/CO = 1/10; molecular sieve 4A 4 g; CH₂Cl₂ 100 ml; Pd(OAc)₂/Co(acac)₃/dmphen/BQ/TBAB = 1/8/5/30/60; Pd(OAc)₂ 0.04 mmol; phenol 0.874 mol dm⁻³.

methyl group since cresols have practically the same reactivity of the phenol (see Tables 5 and 6). It is likely that the steric hindrance, provided by two methyl groups in the neighbor of the hydroxyl group, plays a beneficial role as found for the substituted 1,9-phenanthroline and 2,2'-bipyridyl-Pd complexes [16,20]. 2,4-dichlorophenol, 4-nitrophenol and anisole do not give carbonates.

3.4. Deactivation of the catalytic system

The profile of phenols consumption vs. time suggests that there is a hinderance that limits the conversion (see Figs. 2–5). As a matter of fact, complete phenol conversion is not achieved and the reaction stops after a few hours. Also the consumption of O₂ is not complete, suggesting that the Pd catalyzed CO oxidation to CO₂ stops too

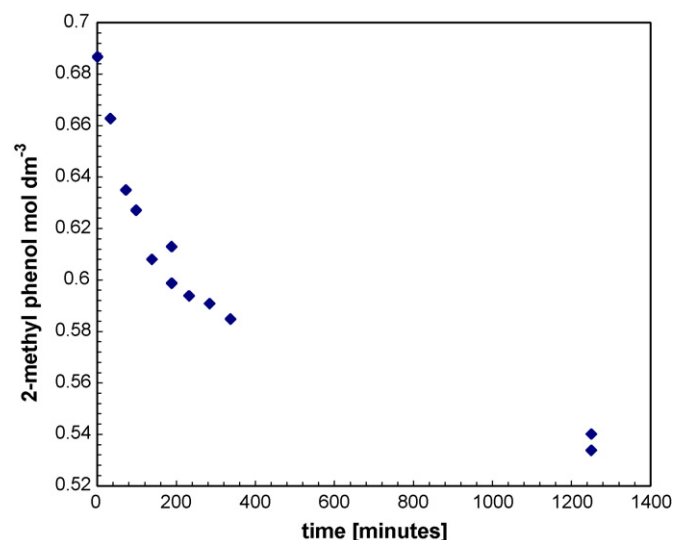


Fig. 3. 2-methylphenol consumption profile. Run conditions: T, 382 K; P, 60 bar; O₂/CO = 1/10; molecular sieve 4A 4 g; CH₂Cl₂ 100 ml; Pd(OAc)₂/Co(acac)₃/dmphen/BQ/TBAB = 1/8/5/30/60; Pd(OAc)₂ 0.04 mmol; 2-methylphenol 0.688 mol dm⁻³.

Table 6
Reactivity of some substituted phenols on conversion and selectivity to diarylcarbonate after 4 h of reaction with solvent in the presence of the catalytic system Pd(OAc)₂-(dmphen). Run conditions: T, 382 K; P, 60 bar; O₂/CO = 1/10; molecular sieve 4A 2 g; CH₂Cl₂ 5 ml; Pd(OAc)₂/Co(acac)₃/dmphen/BQ/TBAB = 1/8/5/30/60; Pd(OAc)₂ 0.01 mmol; phenol 11 mmol.

Substrate	Phenol conversion [%]	Carbonate selectivity [%]	Carbonate yield [%]	TON	TOF [h ⁻¹]
Phenol	20	98	9.8	200	50
2-cresol	22 ^a	70	7.4	154	39
3-cresol	21	90	9.4	198	50
4-cresol	22 ^a	70	7.7	154	39
2,6-di-Mephenol	32	90	14	290	72
4-nitrophenol	5	/	/	/	/
2,4-di-chlorophenol	10 ^b	/	/	/	/
Anisole	/	/	/	/	/

^a Complex mixture in which some products of methyl oxidation has been observed by GC–MS.

^b Complex mixture of products.

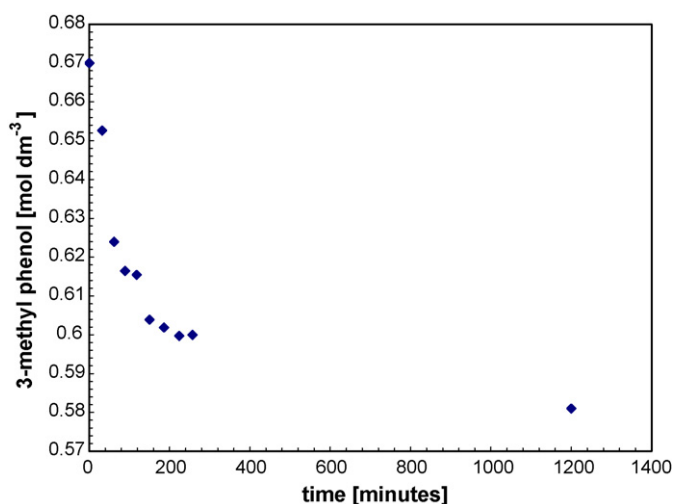


Fig. 4. 3-methylphenol consumption profile. Run conditions: T, 382 K; P, 60 bar; O₂/CO = 1/10; molecular sieve 4A 4 g; CH₂Cl₂ 100 ml; Pd(OAc)₂/Co(acac)₃/dmphen/BQ/TBAB = 1/8/5/30/60; Pd(OAc)₂ 0.04 mmol; 3-methylphenol 0.671 mol dm⁻³.

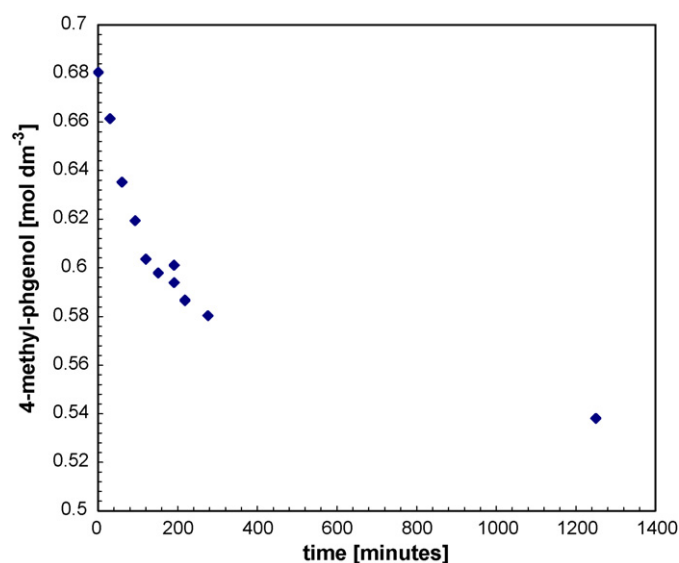


Fig. 5. 4-methylphenol consumption profile. Run conditions: T, 382 K; P, 60 bar; O₂/CO = 1/10; molecular sieve 4A 4 g; CH₂Cl₂ 100 ml; Pd(OAc)₂/Co(acac)₃/dmphen/BQ/TBAB = 1/8/5/30/60; Pd(OAc)₂ 0.04 mmol; 4-methylphenol 0.680 mol dm⁻³.

[9,10]. These evidences suggest that fast catalyst deactivation limits the whole process. Table 7 reports the initial activity ($-r_0$) of the catalytic system Pd(OAc)₂/Co(acac)₃/dmphen/BQ/TBAB = 1/8/5/30/60 on the oxidative carbonylation of different phenols. Small variation of the initial activity but substantial differences on the final conversion and selectivity are observed. As a matter of fact, after 20 h of reaction, 2-cresol and 4-cresol give a conversion twice with respect to phenol and 3-cresol, but a lower selectivity to carbonate. Thus, the methyl group in ortho and para positions increases phenol reactivity, though more with respect to the side reactions, thus lowering the selectivity.

3.5. Activity and selectivity of different Pd catalysts in CH₂Cl₂ in the oxidative carbonylation of phenol

As previously discussed, the oxidative carbonylation of phenols is catalyzed also by heterogeneous catalysts [14,30,31]. As a matter of fact, the nature of the catalytic process and the phase in which

it actually occurs are not clear. Table 8 shows the comparison of different heterogeneous and homogeneous catalytic systems. The best results are obtained by using homogeneous precursors, but the performance of the heterogeneous catalyst is practically comparable. As already suggested, formation of Pd nanoparticles occurs also with homogeneous systems [9,10,14], and this might be the reason why homogeneous and heterogeneous systems show comparable activity. This has been found also for the Pd catalyzed Heck reaction between an arylbromide and an olefin when carried out above 120 °C. Irrespective of the nature of the catalyst precursor, homogeneous, colloidal or heterogeneous, none of these catalysts are stable, they all have a tendency to form soluble Pd colloids or nanoparticles. It was proposed that the arylating agent continuously attacks the Pd atom at the rim of the nanoparticles leading to the formation of soluble intermediates through which the catalytic cycle occurs [27],

Table 7
Activity and selectivity of the Pd(OAc)₂-(dmphen) catalytic system with different phenols in 100 ml CH₂Cl₂. Run conditions: T, 382 K; P, 60 bar; O₂/CO = 1/10; molecular sieve 4A 4 g; CH₂Cl₂ 100 ml; Pd(OAc)₂/Co(acac)₃/dmphen/BQ/TBAB = 1/8/5/30/60; phenol 0.87 mol dm⁻³; Pd(OAc)₂ 0.04 mmol; cresols 0.68 mol dm⁻³.

Substrate	Conversion 4 h [%]	Selectivity 4 h [%]	Conversion 20 h [%]	Selectivity 20 h [%]	$-r_0$ [mol dm ⁻³ min ⁻¹]	Initial TOF [h ⁻¹]
Phenol	8.3	98	11	97	0.0007	11
o-cresol	10	90	23	80	0.0009	14
m-cresol	11	95	13	92	0.0009	14
p-cresol	15	85	22	80	0.0010	16

Table 8

Activity and selectivity on the oxidative carbonylation of phenol in the presence of different Pd precursors. Run conditions: *T*, 382 K; *P*, 60 bar; O₂/CO = 1/10; molecular sieve 4A 4 g; CH₂Cl₂ 100 ml; Pd(OAc)₂/Co(acac)₃/L/BQ/TBAB = 1/8/5/30/60; phenol 0.87 mol dm⁻³; Pd(OAc)₂ 0.04 mmol.

Catalyst	Conversion 4 h [%]	Selectivity 4 h [%]	Conversion 20 h [%]	Selectivity 20 h [%]	$-r_0$ [mol dm ⁻³ min ⁻¹]	Initial TOF [h ⁻¹]
Pd(OAc) ₂ ^a	4.5	98	6.7	97	0.0004	6.3
PdCl ₂ ^a	6.3	98	9.2	97	0.0007	11
Pd/C 0.5% ^{a,b}	4.2	98	8.2	97	0.0004	6.3 ^c
Pd(OAc) ₂ -(dmphen)	8.3	98	10.9	97	0.0007	11
Pd(OAc) ₂ -(trind)	9.1	98	13.8	97	0.0007	11

^a No ligand loaded.

^b Loaded 1.00 g of catalyst.

^c Based on total amount of Pd of the catalyst.

Table 9

Initial activity and selectivity in oxidative carbonylation of phenol in the presence of different ammonium salts, Pd(OAc)₂-(dmphen)catalyst. Run conditions: *T*, 382 K; *P*, 60 bar; O₂/CO = 1/10; molecular sieve 4A 4 g; CH₂Cl₂ 100 ml; Pd(OAc)₂/Co(acac)₃/dmphen/BQ/TBAX = 1/8/5/30/60; Pd(OAc)₂ 0.04 mmol; phenol 0.87 mol dm⁻³.

Ammonium salt (TBAX)	Conversion 4 h [%]	Selectivity 4 h [%]	Conversion 20 h [%]	Selectivity 20 h [%]	$-r_0$ [mol dm ⁻³ min ⁻¹]	Initial TOF [h ⁻¹]
TBAF	8.5	55	11	52	0.0007	11
TBAC	7.1	65	9.5	55	0.0006	9.2
TBAB	8.3	98	11	97	0.0007	11
TBAI	2.9	61	5.2	53	0.0001	1.6

and that if the nanoparticles grow beyond a certain size, palladium black forms and catalysis stops.

Going back to the oxidative carbonylation of phenols, two reasons of catalyst deactivation can be reckoned. In addition to the increase of the Pd nanoparticles, it might be also that the active sites are blocked by the adsorption of phenols, which are known to form from phenols. The role of TBAB should be connected with the formation-stabilization of Pd nanoparticles, impeding their growth to less active Pd black [9,10,14]. This is, however, a conjecture which cannot explain the different behavior of the tetrabutylammonium salts with different halogenides, as shown in Table 9. TBAB is the only one that gives high selectivity in DPC (95–98%) suggesting an important role of the halogenide itself.

In Fig. 6 the influence of the amount of catalyst on the reaction rate and the yield in DPC is shown. It appears that the yield in DPC increases linearly with Pd increasing, whereas the rate is poorly influenced. Such an anomalous behavior is probably due

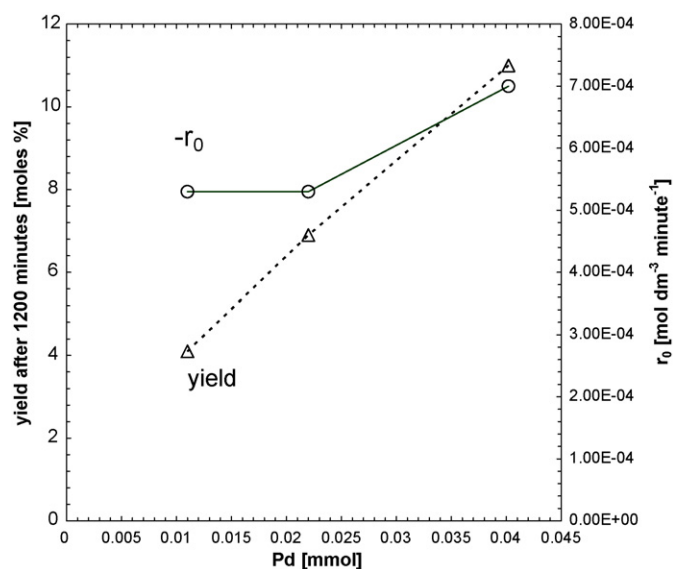


Fig. 6. Influence of the catalyst amount on the initial activity and on the yield after 20 h of reaction. Run conditions: *T*, 382 K; *P*, 60 bar; O₂/CO = 1/10; molecular sieve 4A 4 g; CH₂Cl₂ 100 ml; Pd(OAc)₂/Co(acac)₃/dmphen/BQ/TBAB = 1/8/5/30/60; Pd(OAc)₂ 0.01–0.04 mmol; phenol 0.68 mol dm⁻³.

to the extensive catalyst deactivation which practically determines the overall rate of reaction. For the same reason, the yield in DPC increases linearly with the catalyst amount, in fact, the number of catalytic cycle of the each Pd atom is constant thus the yield is proportional to its amount.

4. Conclusions

This paper gives some new insights on the reaction steps, which are summarized as follows:

- (1) different catalytic systems, both homogeneous and heterogeneous, shows, comparable yields and selectivities in DPC after 4 h of reaction, whereas after 20 h only Pd(OAc)₂/trind/Co(acac)₃/TBAB and Pd(OAc)₂/dmphen/Co(acac)₃/TBAB catalytic systems allow an yield increase;
- (2) the roles of the ligands and of TBAB are not simply related to the formation of Pd catalytic intermediates in homogeneous phase but also with the stabilization of Pd nanoparticles, thus easing their reoxidation to Pd(II) species;
- (3) kinetic measurements using different mono-substituted methyl phenols show a negligible effect of the a substituent on the overall rate of reaction, but an important one on the selectivity. Reactivity of 2,6-dimethylphenol is twice that of phenol and of methylphenols suggesting that steric hindrance plays a beneficial role;
- (4) final conversion and reaction rate are determined also by the fast catalyst deactivation.

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