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A new efficient Pd-catalyzed synthesis of diphenyl carbonate with heteropolyacid as a cocatalyst

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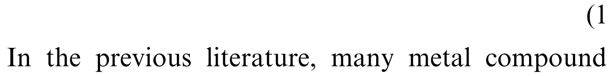
Abstract

A new catalytic system, Pd–Mn-HPA (heteropolyacid), has been found to be very efficient in the oxidative carbonylation of phenol to diphenyl carbonate (DPC) with CO and oxygen at low pressure in the absence of solvent. Synergistic effect between W–Mo–heteropolyacid and $Mn(OAc)_2$ was observed for regenerating the Pd(II) species from Pd(0). The ratio of W–Mo in heteropolyacid, efficiency of the heteropolyacid salts and the roles of tetrabutylammonium bromide and molecular sieves have been investigated in detail. Using suitable components of the catalyst system, 53% yield of DPC with a Pd turnover number of 827 can be attained. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Heteropolyacid; Diphenyl carbonate; Phenol; Oxidative carbonylation; Synergistic effect

1. Introduction

Diphenyl carbonate (DPC), an important precursor of polycarbonates, is industrially obtained from phosgenation of phenol, accompanied by the formation of chlorinated waste [1]. In recent years, there has been an increasing demand for a safer and environmentally benign process for the DPC synthesis. Oxidative carbonylation of phenol with CO and oxygen in one-step is an attractive process for the synthesis of DPC, where H_2O is the sole byproduct and the use of highly toxic phosgene can be avoided Eq. (1):



$$\mathrm{PhOH} + \mathrm{CO} + \mathrm{O_2} \xrightarrow{\mathrm{Cat}} \mathrm{PhO{-}\overset{O}{\overset{\|}{C}}{-}OPh} + \mathrm{H_2O} \tag{1}$$

In the previous literature, many metal compounds were chosen as catalysts for the oxidative carbonylation reaction [2–10], and palladium was thought to be the most active. In this reaction, the efficient regeneration of the Pd(II) species from Pd(0) is the crucial step for the high yield of DPC and high turnover number (TON) of Pd. However, direct oxidation of Pd(0) to the Pd(II) species with oxygen was confirmed to be very slow, which results in an aggregation of Pd(0) to form Pd black, which is more difficult to be reoxidized to the Pd(II) species than Pd(0). Therefore, the efficient redox cocatalysts are essential to achieve rapid reoxidation of Pd(0). In the Wacker process [11], copper salts were chosen to regenerate Pd(II) with high efficiency. In the DPC synthesis reaction, the efficiency of palladium is lower than that in the Wacker process when copper salts were used [6]. Until now, the catalytic system with high efficiency is very scare, and the systems with higher yield of DPC and higher efficiency of Pd are usually run under high pressure or crucial reaction conditions. From the industrial point of view, it is necessary to seek a novel catalytic system with high efficiency that can be performed under mild conditions. Heteropolyacids are broadly utilized in the catalytic reactions because of their high stability and redox reversibility. It was reported that heteropolyacids could act as the redox cocatalysts in the some palladium-catalyzed reactions [12,13]. Recently, we reported a heteropolyacid-catalyzed partial oxidation of methane [14]. Using heteropolyacid as cocatalyst, we investigated the synthesis of DPC by the oxidative carbonylation of phenol with the $Pd(OAc)_2$ catalyst under low pressure in the absence of solvent. A part of this work has appeared in a preliminary communication [15]. Here,

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we report the details of this heteropolyacid-assisted oxidative carbonylation reaction.

2. Results and discussion

2.1. *Efficiency of oxidative carbonylation with various heteropolyacid cocatalysts*

In a flow system and under low pressure, some heteropolyacids have been investigated as the redox cocatalysts for the oxidative carbonylation of phenol to DPC with the $Pd(OAc)_2$ catalyst in the absence of solvent. The results are summarized in Table 1. From the data in Table 1, one can see that, without redox cocatalyst in the system, $Pd(OAc)_2$ is also slightly active for the oxidative carbonylation of phenol to DPC, although the yield of DPC is only 0.3% based on phenol with TON of 5 based on Pd after 3 h (entry 1). These results show that the regeneration of Pd(II) species from Pd(0) with oxygen is a slow reaction under the present conditions. In the present work, a 1.4% yield can be obtained with TON of 22 when $H_3PVMo_{11}O_{40}$ is used as the cocatalyst (entry 2). $H_5PV_2Mo_{10}O_{40}$ is more active than $H_4PVMo_{11}O_{40}$; yield can be improved to 4.4% with a TON of 69 (entry 3). $H_3PW_6Mo_6O_{40}$ is inactive as the cocatalyst (entry 4), which means that $H_3PW_6Mo_6O_{40}$ is incapable of regenerating the Pd(II) species from Pd(0) under the present conditions, although in previous literature [16], the $PdSO_4$–$H_3PW_6Mo_6O_{40}$ catalyst showed good activity in the oxidation of cyclic olefins to the corresponding cyclic ketones with oxygen in the aqueous solution. $Mn(OAc)_2$ is a good cocatalyst, and yield can reach 12.9% with a TON of 202 (entry 5). In all cases, the major side products are phenysalicylate and 4-phenoxy phenol, which have been identified by the GC-MS spectra. Control experiments show that, the side products are not formed from a subsequent reaction of DPC, and that the DPC can be slightly hydrolyzed to phenol and carbon dioxide under the reaction conditions.

Interestingly, the combinations of some P–Mo–W-containing heteropolyacids with $Mn(OAc)_2$ as the bicomponent cocatalyst give higher yields than with $Mn(OAc)_2$ as the sole cocatalyst (entries 6 and 7). Particularly, yield can be improved to 18.9% with TON of 295 when $H_3PW_6Mo_6O_{40}$ is combined with $Mn(OAc)_2$ as the cocatalyst (entry 7), despite the fact that $H_3PW_6Mo_6O_{40}$ as the sole cocatalyst is inactive. A low yield (13.1%) is obtained with $Mn(OAc)_2$ combined with simple $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ as the cocatalyst (entry 9). These results probably suggest that, there is the synergistic effect existing between $Mn(OAc)_2$ and some P–W–Mo-containing heteropolyacids for regenerating the Pd(II) species. Although $H_3PW_6Mo_6O_{40}$ is inactive under the present conditions, it can assist the regeneration of the Pd(II) species with high efficiency when it is combined with $Mn(OAc)_2$ as the bicomponent cocatalyst. In addition, $H_4SiW_6Mo_6O_{40}$ shows the same activity as those of the P–W–Mo-containing heteropolyacids (entry 10). The synergistic effect was not observed when the combination of vanadium-containing heteropolyacids with $Mn(OAc)_2$ as the bicomponent cocatalyst was used (entry 11).

2.2. *Effect of the ratio of W–Mo in heteropolyacid*

The influence of the ratio of W–Mo in heteropolyacids ($H_3PW_xMo_{12-x}O_{40}$) on the catalytic activity is

Table 1
Oxidative carbonylation of phenol to DPC with various heteropolyacids as a cocatalyst [a]

Entry	Cocatalyst	DPC yield (%) [b]	TON [c]	DPC selectivity (%) [d]
1	–	0.3	5	>99.9
2	$H_4PVMo_{11}O_{40}$	1.4	22	99
3	$H_5PV_2Mo_{10}O_{40}$	4.4	69	97.4
4	$H_3PW_6Mo_6O_{40}$	0.4	6	>99.9
5	$Mn(OAc)_2$	12.9	202	97
6	$H_3PW_{11}MoO_{40}+Mn(OAc)_2$	16.4	256	97.5
7	$H_3PW_6Mo_6O_{40}+Mn(OAc)_2$	18.9	295	97
8	$H_3PW_4Mo_8O_{40}+Mn(OAc)_2$	12.4	194	96.8
9	$H_3PW_{12}O_{40}+H_3PMo_{12}O_{40}+Mn(OAc)_2$ [e]	13.1	205	98.0
10	$H_4SiW_6Mo_6O_{40}+Mn(OAc)_2$	18.2	284	97.4
11	$H_5PV_2Mo_{10}O_{40}+Mn(OAc)_2$	10.2	159	98.6

[a] Phenol 0.5 mol, $Pd(OAc)_2$ 0.16 mmol, $Mn(OAc)_2$ 0.32 mmol, heteropolyacid 0.047 mmol, tetrabutylammonium bromide 3 mmol, M.S. 7 g, 8 atm, CO 500 ml min^{-1}, O_2 35 ml min^{-1}, 80 °C, 3 h.

[b] GC yield based on charged phenol.

[c] TON based on Pd.

[d] DPC percentage in the products evaluated from the peak areas on GC and the products identified by GC-MS spectroscopy.

[e] $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$, 0.03 mmol, respectively.

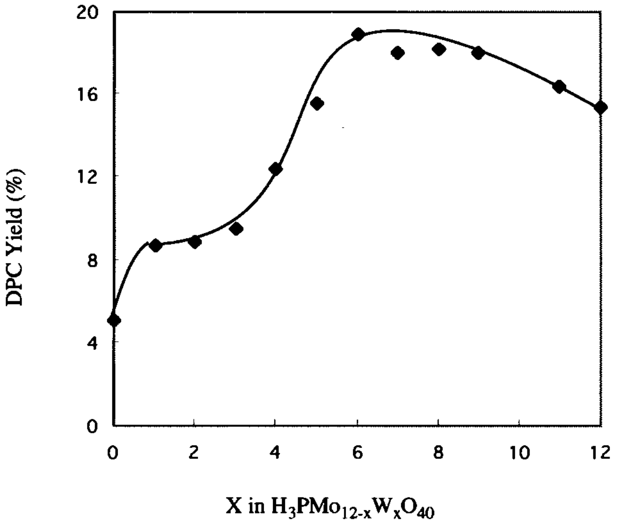


Fig. 1. The influence of the ratio of W–Mo in $H_3PW_xMo_{12-x}O_{40}$ on the reaction. Conditions: phenol (0.5 mol); $Pd(OAc)_2$ (0.16 mmol); $Mn(OAc)_2$ (0.32 mmol); heteropolyacid (0.047 mmol); tetrabutylammonium bromide (3 mmol); M.S. (7 g), pressure (8 atm); CO (500 ml min^{-1}); O_2 (35 ml min^{-1}); 80 °C; 3 h.

shown in Fig. 1. The combination of $H_3PMo_{12}O_{40}$ ($x = 0$) with $Mn(OAc)_2$ as the bicomponent cocatalyst gives only a 5% yield. Yield can increase remarkably with heteropolyacids containing W and Mo. A satisfactory yield of 18.9% can be obtained when the ratio of W–Mo is 6:6 ($x = 6$). The yield drops to 15% when $H_3PW_{12}O_{40}$ ($x = 12$) is used as one of the cocatalysts. Thus, judging from the no synergistic effect of a simple mixture of $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ (Table 1, entry 9), the presence of polyanions with W–Mo-mixed additional atoms is responsible for improving the yield. It has been reported that the redox potential and catalytic performance can be changed by the W–Mo mixed coordination ($H_3PW_xMo_{12-x}O_{40}$) [17]. Therefore, the synergistic effect is likely to be associated with the change in the redox properties of the polyanions.

2.3. *Effect of tetrabutylammonium bromide*

Tetrabutylammonium bromide (TBAB) is neither a catalyst for the oxidative carbonylation of phenol, nor a cocatalyst for the regeneration of the Pd(II) species. However, it is very essential for the catalytic system (Table 2). Only a trace amount of the product is formed (entry 1) without the addition of TBAB in the reaction mixtures. Higher yield of DPC (14.4%) can be obtained with 0.75 mmol TBAB, and the yield can reach 22.1% with TON of 345 when 4.5 mmol TBAB are added in the reaction mixtures. It was thought that, the reaction of ammonium halide and phenol could produce ammonium phenoxide which was advantageous for the coordination of phenol to the Pd(II) species in the oxidative carbonylation process [2,5]. In addition, in the previous patents [11,18], sodium phenolate added to the reaction mixtures could improve the yield of DPC. However, under the present conditions, yield of DPC decreases sharply to 1.7% and a considerable amount of benzoquinone is formed in the reaction when sodium phenolate is added to the reaction mixtures (entry 6). Probably sodium phenoxide makes the oxidization of phenol to benzoquinone easy and causes the decrease in DPC. However, the role of TBAB is still not clear although it improves the reaction greatly.

2.4. *The role of molecular sieves*

It was confirmed by the control experiments that water could react with DPC (hydrolysis) to produce phenol and CO_2. Thus, 3 A powder molecular sieves (M.S.) are added to remove water formed during the reaction. The results are listed in Table 3. In the present catalytic system, without M.S. added to the reaction mixtures, yield is only 0.5% (entry 1). When 14 g M.S. are added to the reaction mixtures, yield was improved to 19.3% with TON of 301 (entry 4). However, putting too many M.S. to the reaction mixtures can cause a

Table 2
Effect of tetrabutylammonium bromide on the catalytic system [a]

Entry	Tetrabutylammonium bromide (mmol)	DPC yield (%) [b]	TON [c]	DPC selectivity (%) [d]
1	–	Trace		
2	0.75	14.4	225	98.2
3	1.5	19.2	300	99.3
4	3.0	18.9	295	97
5	4.5	22.1	345	>99.9
6	3.0 [e]	1.7 [f]	27	97

[a] Phenol 0.5 mol, $Pd(OAc)_2$ 0.16 mmol, $Mn(OAc)_2$ 0.32 mmol, $H_3PW_6Mo_6O_{40}$ 0.047 mmol, M.S. 7 g, 8 atm, CO 500 ml min^{-1}, O_2 35 ml min^{-1}, 80 °C, 3 h.

[b] GC yield based on charged phenol.

[c] TON based on Pd.

[d] DPC percentage in the products evaluated from the peak areas on GC and the products identified by GC-MS spectroscopy.

[e] Sodium phenolate 4.7 mmol added.

[f] A considerable amount of benzoquinone was obtained.

Table 3
Effect of M.S. on DPC yield [a]

Entry	M.S. (g)	DPC yield (%) [b]	TON [c]	DPC selectivity (%) [d]
1	–	0.5	8	97
2	3.5	8.6	134	96.1
3	7	18.9	295	97
4	14	19.3	301	98.2
5	28	5.4	84	85.9
6	$Pd(OAc)_2$/M.S. (1 g)	1.2	19	90.2
7	$Pd(OAc)_2$/M.S. (1 g)+M.S. (7 g)	20.5	320	99.5
8	7 [e]	0.8	12	95.2
9	Na_2SO_4 (7 g)	0.4	6	97

[a] Phenol 0.5 mol, $Pd(OAc)_2$ 0.16 mmol, $Mn(OAc)_2$ 0.32 mmol, $H_3PW_6Mo_6O_{40}$ 0.047 mmol, tetrabutylammonium bromide 3 mmol, 3 A powder M.S. used, 8 atm, CO 500 ml min^{-1}, O_2 35 ml min^{-1}, 80 °C, 3 h.

[b] GC yield based on charged phenol.

[c] TON based on Pd.

[d] DPC percentage in the products evaluated from the peak areas on GC and the products identified by GC-MS spectroscopy.

[e] 3 A pellets M.S. used.

decrease in the activity of the catalytic system; only 5.4% yield is obtained with 28 g M.S. (entry 5). A decrease in the DPC yield by adding too many M.S. is possibly because these M.S. make the molten phenol very viscous, decreasing the chance of reoxidation of Pd(0) by the cocatalyst. Using supported catalyst, $Pd(OAc)_2$–M.S., only 1.2% yield is obtained with 90.2% selectivity (entry 6). However, when combining the supported catalyst with 7 g M.S., the yield can be improved to 20.5% with 99.9% selectivity (entry 7). Further, when powder M.S. is used in the reaction, less than 1 ppm palladium could be detected in the reaction solution after the reaction (entry 8), indicating that all the palladium was precipitated to M.S. during the course of the reaction. However, when 7 g pellets M.S. are used as the dehydrating agent, yield is only 0.8%. In addition, when anhydrous Na_2SO_4, which cannot act as a support for $Pd(OAc)_2$, is used as the dehydrating agent, yield is only 0.4% (entry 9). This may be because of the surface-active effects but may also simply be because of the fact that it is a far less active dehydrating agent than the fully activated M.S. All these results clearly suggest that the M.S. acts both as a support to Pd and as the dehydrating agent in the reaction.

2.5. Time course of oxidative carbonylation

Time course of oxidative carbonylation is shown in Fig. 2. The DPC yield increases obviously with an increasing the reaction time for the first 5 h after ehich the yield increases slow down. After 9 h, a 31.7% yield of DPC can be obtained with a TON of 495. Yield can be improved to 37.3% with TON of 583 when the gas flow rate is increased from CO (500 ml min^{-1}) and O_2 (35 ml min^{-1}) to CO (670 ml min^{-1}) and O_2 (47 ml min^{-1}), which suggests that the efficiency of the palladium catalyst is influenced greatly by the gas flow rate. This is in good agreement with the report that high TON of Pd is usually obtained under high pressure (high gas concentration in the reaction solution) [3,8]. Probably, low gas flow rate of oxygen is insufficient for the regeneration of the Pd(II) species in time.

2.6. Efficiency of salts of heteropolyacids as cocatalyst

Oxidative carbonylation of phenol with salts of heteropolyacids combined with $Mn(OAc)_2$ as the bicomponent cocatalyst has also been investigated. The results are summarized in Table 4. Under the same reaction conditions, activities of ammonium salts of heteropolysacids are generally higher than those of the heteropolyacids as the cocatalysts (entries 1–3). $(TBA)_4SiW_6Mo_6O_{40}$ (TBA: tetrabutylammonium) as one of the cocatalysts gives 22.7% yield of DPC with TON of 354. At the gas flow rate of CO (670 ml min^{-1}) and O_2 (47 ml min^{-1}), yields can reach 41.2

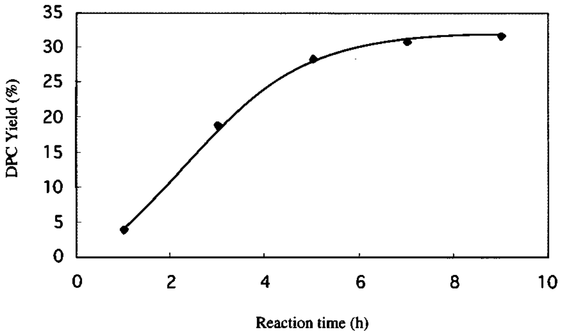


Fig. 2. Time course of oxidative carbonation. Conditions: phenol (0.5 mol); $Pd(OAc)_2$ (0.16 mmol); $Mn(OAc)_2$ (0.32 mmol); $H_3PW_6Mo_6O_{40}$ (0.047 mmol); tetrabutylammonium bromide (3 mmol); M.S. (7 g); pressure (8 atm); CO (500 ml min^{-1}); O_2 (35 ml min^{-1}); 80 °C.

Table 4
Oxidative carbonylation of phenol to DPC with various salts of heteropolyacids as a cocatalyst [a]

Entry	Salts of heteropolyacids	DPC yield (%) [b]	TON [c]	DPC selectivity (%) [d]
1	$(TBA)_3PW_6Mo_6O_{40}$	20.8	325	99.2
2	$(TBA)_4SiW_6Mo_6O_{40}$	22.7	354	99.5
3	$(TBA)_4SiWMo_{11}O_{40}$	20.8	325	99
4	$(TBA)_3PW_6Mo_6O_{40}$ [e]	29.5	460	98.9
5	$(TBA)_4SiW_6Mo_6O_{40}$ [e]	41.2	643	99.4
6	$(TBA)_4SiWMo_{11}O_{40}$ [e]	43.8	684	99.7
7	$(TBA)_4SiWMo_{11}O_{40}$ [f]	53	827	99.8
8	$PdHPW_6Mo_6O_{40}$ [g]	10.5	164	99
9	$PdH_2SiW_6Mo_6O_{40}$ [g]	11.7	175	97.4
10	$PdH_2SiMo_{12}O_{40}$ [g]	10.3	161	98

[a] Phenol 0.5 mol, $Pd(OAc)_2$ 0.16 mmol, $Mn(OAc)_2$ 0.32 mmol, salt of heteropolyacid 0.047 mmol, tetrabutylammonium bromide 3 mmol, M.S. 7 g, 8 atm, CO 500 ml min^{-1}, O_2 35 ml min^{-1}, 80 °C, 3 h.

[b] GC yield based on charged phenol.

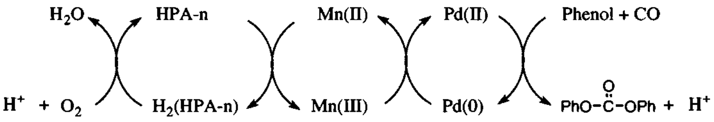
[c] TON based on Pd.

[d] DPC percentage in the products evaluated from the peak areas on GC and the products identified by GC-MS spectroscopy.

[e] CO 670 ml min^{-1} and O_2 47 ml min^{-1}, 9 h.

[f] Tetrahydrofuran 15 ml added, CO 670 ml min^{-1} and O_2 47 ml min^{-1}, 9 h.

[g] Salt of heteropolyacid 0.16 mmol, without $Pd(OAc)_2$.



Scheme 1. A possible mechanism for the oxidative carbonylation of phenol with CO and oxygen with Pd–Mn–HPA catalyst system.

and 43.8% with TON of 643 and 684 after 9 h, when $(TBA)_4SiW_6Mo_6O_{40}$ and $(TBA)_4SiWMo_{11}O_{40}$ were used as the cocatalysts, respectively (entries 5 and 6). Further, the yield of DPC can be improved up to 53% with TON of 827 when 15 ml tetrahydrofuran are added as the solvent in the reaction mixture (entry 7). Probably, tetrahydrofuran added as the solvent can decrease the viscosity of the reaction solution and increase the chance of regeneration of the active Pd species by the cocatalyst. To the best of our knowledge, the present catalytic system is the first one in which heteropolyacids (HPA) are used as the cocatlysts to give good results in the synthesis of DPC, and the efficiency of present catalytic system is higher than most of the reported catalytic systems for the oxidative carbonylation. Further, in this system, higher yield of DPC with a higher efficiency of Pd is attained under low pressure. However, low yields were obtained when palladium salts of heteropolyacids are used as the catalysts (entries 8–10).

2.7. Multistep electron transfer catalytic cycle

The results in Table 1 show that there is a synergistic effect existing between some heteropolyacids and $Mn(OAc)_2$ for the regeneration of the Pd(II) species. A possible mechanism of the multistep electron transfer is proposed in Scheme 1. The Pd(II) species would be reduced to Pd(0) during the DPC formation from two molecules of phenol and one molecule of CO. The Pd(0) thus formed would then be reoxidized by Mn(III) to form Pd(II) and Mn(II), and in turn Mn(II) would be reoxidized to Mn(III) by heteropolyacid (HPA-*n*) which is thus reduced to H_2(HPA-*n*). Finally, H_2(HPA-*n*) would be oxidized to HPA-*n* by O_2.

3. Conclusions

Heteropolyacids, combined with $Mn(OAc)_2$ as the bicomponent cocatalyst, were found to assist in the oxidative carbonylation of phenol with CO and oxygen to diphenyl carbonate (DPC) with $Pd(OAc)_2$ as the catalyst under low pressure and in the absence of solvent. The efficient synergistic effect for regenerating the Pd(II) species from Pd(0) is observed when some heteropolyacids are combined with $Mn(OAc)_2$ as the bicomponent cocatalyst. Tetrabutylammonium bromide and M.S. are essential for the efficient oxidative carbonylation, and M.S. act as both the dehydrating agent and a support for palladium. Tetrabutylammonium salts of heteropolyacids usually show higher efficiencies in regenerating the Pd(II) species than heteropolyacids, respectively. Under the present conditions, 53% yield of

DPC based on phenol can be obtained with a Pd TON of 827.

4. Experimental

Salts of heteropolyacids were gifted generously from Teijin Ltd. All other reagents were obtained from commercial sources and used as received. Molecular sieves (M.S.) were activated at 450 °C in air for 10 h before use. All the reactions are run in a flow system.

A typical reaction procedure is as follows: $Pd(OAc)_2$ 0.036 g (0.16 mmol), $Mn(OAc)_2 \cdot 4H_2O$ 0.078 g (0.32 mmol), heteropolyacid 0.047 mmol, tetrabutylammonium bromide 1 g (3 mmol), 3 A powder M.S. 7 g and hot phenol 47 g (0.5 mol) were charged in a 100 ml stainless steel autoclave which was kept at 60 °C. The autoclave was then sealed. With mechanical stirring at 800 rpm, a gas mixture (6.5 mol% O_2 and 93.5 mol% CO) was introduced into the autoclave at a flow rate of 535 ml min^{-1} and the autoclave was heated to 80 °C. The pressure of the autoclave was kept at 8 atm with continuous gas flow for the desired time. After the reaction, the pressure was reduced to the atmospheric pressure, and the gas mixture was exchanged with nitrogen. Next, the hot reaction solution was removed into a receiver and 30 ml EtOAc were used to wash the autoclave. Finally, the solutions were combined and analyzed by GC with a capillary column (DB-1, 15 m × ∅ 0.53 mm, J & W Scientific). The products were identified by GC-MS spectra. The major side products were phenysalicylate and 4-phenoxy phenol. The yield of DPC is based on the charged phenol and determined by GC using diphenyl as an internal standard and is listed in the tables. The selectivity is based on the DPC percentage in the products evaluated from the peak areas on the GC chart.

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