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A new heterogeneous catalyst for the oxidative carbonylation of phenol to diphenyl carbonate

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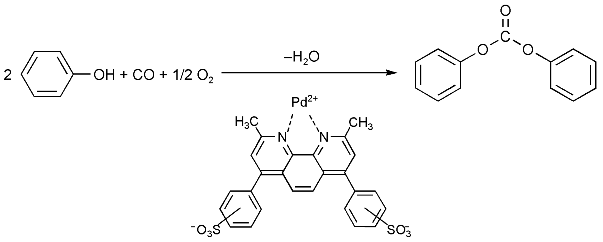
Using layered double hydroxides as a support, both the palladium catalyst and the cobalt co-catalyst are heterogenised and proven to form an acceptable catalytic system for the heterogeneous oxidative carbonylation of phenol to diphenyl carbonate (DPC).

In the current search for environmentally benign and sustainable processes, oxidative carbonylation of phenol is a promising alternative that avoids the use of phosgene in the one-step synthesis of diphenyl carbonate (DPC), which is an important precursor for polycarbonates.[1] Since oxygen is used as final oxidant, the only waste product is H_2O (Scheme 1).

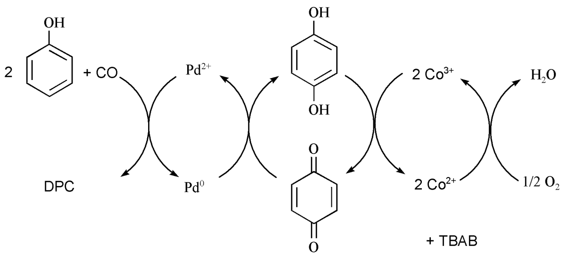


Scheme 1 Oxidative carbonylation of phenol to diphenyl carbonate.

In this Wacker-type reaction involving the Pd^{2+}/Pd^0 redox couple, the key problem is to avoid clustering of zerovalent Pd. Its reoxidation, generally done indirectly with oxygen and realised by means of an electron transfer chain consisting of a combination of two or more metallic and/or organic co-catalysts (Scheme 2), is favoured by stabilising the Pd species through interaction with a chelating ligand.[2] In particular, substituted phenanthroline ligands are shown to have a positive influence on the catalyst performances in the oxycarbonylation of phenol.[3]

Although recently promising results were published in patent literature for the oxidative carbonylation of phenol in homogeneous conditions,[4] effective recovery of the used metals remains a critical item. Therefore, the goal of our work was to develop a heterogeneous catalytic system that combines good catalytic performance with satisfactory recovery of the metals used.

Pd^{2+} ligated with the disodium salt of (2,9-dimethyl)(4,7-diphenylsulfonic acid)-1,10-phenanthroline (BC-SO_3; Scheme 1), was anion exchanged with charge compensating nitrate anions of a layered double hydroxide (LDH).‡ LDH materials with the composition used are known for their basic properties.[5] Considering the importance of phenol activation by formation of the phenoxide ion,[6] such supports could be very beneficial for this chemistry. The dual role of the LDH as base and support for the metallic part(s) of the catalytic system has the additional advantage of bringing the activated substrate and the catalytic sites in close proximity.



Scheme 2 Electron transfer chain between Pd and O_2 used in this work.†

Initially, the supported catalyst was tested under conditions optimised for homogeneous catalysis.[3] Only 30% of the activity obtained homogeneously could be reached (entries 1 and 2, Table 1). However, lowering the amount of Pd present in the reaction medium resulted in a significant increase in the catalytic activity of the system (entries 2–8, Table 1). Maximum turnover frequencies of 387 h^{-1} were obtained. Most likely, the contact between Pd and other members of the electron transfer chain (Co, benzoquinone) responsible for its reoxidation is reduced upon immobilisation of the catalyst on the LDH support, requiring higher relative ratios of those compounds for optimal performance of the catalytic system.

Table 1 also shows for each reaction the amount of Pd leached into solution as determined by AAS. For the lower relative concentrations of Co/Bq/TBAB (entries 2–6) leaching of Pd is limited to less than 5% of the initial amount, corresponding to absolute amounts ranging from 20 to 50 nmol of Pd. Possibly, at higher relative concentrations of benzoquinone and TBAB, the interaction of Pd with benzoquinone and TBAB competes with that of the LDH. Benzoquinone can function as a ligand for Pd^{2+},[7] while TBAB is known to stabilise Pd^0 through formation of metal clusters.[8,9]

The introduction of the basic support reduces the DPC selectivity typically to 95%, favouring the formation of phenoxyphenol as a by-product. In homogeneous catalysis this drop in selectivity is also observed when a copper co-catalyst is used instead of cobalt.[8] The influence of the support composition on reaction rate and selectivity is currently under investigation. As both parameters seem to be affected in an opposite way, determination of the optimal LDH composition is crucial.

Table 1 Effect of different molar ratios of the individual components in the catalytic system for phenol oxidative carbonylation on the DPC productivity and Pd leaching[a]

entry	μmol Pd	Pd/Co/Bq/TBAB/phenol	TOF (h^{-1})	% Pd leached
1[b]	11.0	1/3/30/60/8000	110	—
2	2.06	1/3/30/60/8000	34	2.8
3	1.03	1/6/60/120/16000	55	4.6
4	0.69	1/9/90/180/24000	62	4.3
5	0.52	1/12/120/240/32000	170	4.4
6	0.52	1/12/120/240/32000	136	3.4
7	0.41	1/15/150/300/40000	280	9.2
8	0.34	1/18/180/360/48000	387	16.9
9	0.26	1/24/240/480/64000	296	18.5
10[c]	0.52	1/60/120/240/32000	65	4.1

[a] Reaction conditions: T = 100 °C, t = 3 h, P_{tot} = 55 bar (at RT), CO/O_2 = 10/1. [b] Homogeneous conditions (ref. 3) [c] Supported Co co-catalyst used (see text).

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Finally, the heterogenisation of the second metal component of the system was attempted. Therefore, the anionic Co species, $CoCl_4^{2-}$ was synthesised and ion-exchanged on a $MgAlNO_3$ LDH following literature procedures.[10]§

Preliminary tests with an anchored co-catalyst show very promising results (entry 10, Table 1) as far as activity and degree of leaching is concerned. Pd leaching is less than 5% (21 nmol), while Co leaching was determined to be only 0.5% of the initial amount. It has been certified that in the conditions of entry 2 (Table 1), the solid after filtration could be re-used.

In conclusion, it is shown that the immobilisation of a Pd–BC–SO_3 complex on a MgAl LDH by anion exchange results in a solid catalyst for the oxidative carbonylation of phenol that in terms of activity is superior to the best homogeneous analogues. Whereas Pd leaching is dependent on the relative concentration of the other members in this complex catalytic system, it can be reduced to losses of no more than 30 nmol. Although the electron transfer chain needed to reoxidise Pd is a complex system with components in a very delicate balance, we succeeded in immobilising *via* a similar procedure the second inorganic component of this system as well.

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Notes and references

† TBAB = tetrabutylammonium bromide; $Co(acac)_3$ used.

‡ $MgAlNO_3$ LDH was synthesised by coprecipitation in conditions of supersaturation and at a constant pH of 9.5 ± 0.2 (precursors: $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$; titration with 1 M NaOH). Its structure is confirmed by X-ray analysis while the molar ratio [Mg/Al] is determined to be 1.95 (ICP analysis). IR measurement shows the presence of exchangeable nitrate anions [$\nu_3(NO_3^-)$: 1380 cm^{-1} (s); $\nu_1 + \nu_4$ (NO_3^-): 1786 cm^{-1} (w)].

Prior to ion exchange (24 h; 60 °C), equimolar quantities (0.32 mmol/g LDH) of $Pd(NH_3)_4Cl_2$ and BC-SO_3 were mixed in 100 ml decarbonated bidistilled water to induce complex formation (1 h; 60 °C). Washing of the solid and its lyophilisation are the last steps in the synthesis of the catalyst. The final catalyst contained 70 μmol Pd/g and 0.22 mmol BC-SO_3/g, as determined by ICP analysis and UV–Vis spectroscopy, respectively.

§ To a deep blue solution of 2.2 g of $[Et_4N]_2[CoCl_4]$ in 30 ml of nitromethane, 1 g of the above-described $MgAlNO_3$ LDH was added. The slurry was then stirred for 18 h at room temperature, filtered and washed repeatedly with CH_3NO_2 until no blue colour remained in the filtrate.[10] Finally, the resulting material was dried at room temperature. According to ICP measurements the catalyst contained 0.93 mmol/g Co.

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