

Palladium complexes anchored on silica functionalized by 1,2-diaminocyclohexane: Preparation and catalytic application

Guozhi Fan, Jiao Huang, Zhiqiang Li, Tao Li, Guangxing Li*

Department of Chemistry, Huazhong University of Science and Technology, Wuhan 430074, PR China

Received 23 May 2006; received in revised form 27 October 2006; accepted 3 November 2006

Available online 10 November 2006

Abstract

Palladium complexes anchored on silica functionalized by 1,2-diaminocyclohexane were prepared using the sol–gel technique and used as catalysts in the oxidative carbonylation of phenol to diphenyl carbonate (DPC). The effects of different reaction parameters such as solvent, inorganic cocatalyst, palladium loading and the molar ratio of phenol to Pd on the oxidative carbonylation were studied in detail. Cu_2O and tetrahydrofuran (THF) were found to be the best inorganic cocatalyst and solvent in terms of higher yield of DPC, lower palladium leaching in solution, and fewer byproducts. The yield of DPC and TON reached 12.0% and 60 mol DPC/mol Pd in the presence of Cu_2O and THF, and Pd leaching was only 3.0%. The heterogeneous catalysts revealed higher catalytic activity compared with the homogeneous catalysts. The existence of Pd(0) in the catalytic cycle was confirmed by XRD, and a possible mechanism for the oxidation carbonylation of phenol to DPC in the presence of Cu_2O and heterogeneous catalyst was also proposed.

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Keywords: Supported palladium catalyst; Phenol; Oxidative carbonylation; Diphenyl carbonate

1. Introduction

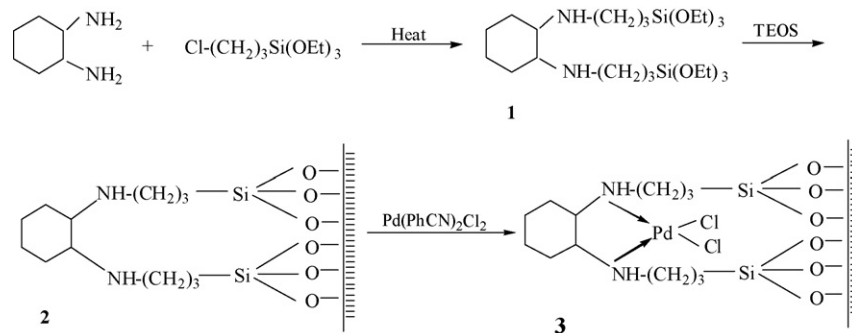
Oxidative carbonylation of phenol with carbon monoxide and oxygen to diphenyl carbonate (DPC) has attracted great interest and is considered as one of the most likely routes to prepare DPC without employing toxic phosgene, H_2O being the sole byproduct. However, the oxidative carbonylation of phenol to DPC has usually been catalyzed by a Pd complex/redox cocatalysts/ammonium halide system in the homogeneous system [1–15]. As is the case of all homogeneous catalysts, there are some problems in the difficulty of separation of the noble metal catalyst and the product.

The immobilization of metal complexes, acting as catalysts, is a field of growing interest. Such systems are able to combine the adjustable selectivity and activity of a homogeneous catalyst with the re-usability of a heterogeneous catalyst [16]. To facilitate the recovery of the noble palladium catalyst in the

homogeneous reactions, palladium complexes anchored on supports such as polystyrene [17], starch [18], SiO_2 [3], zeolites [19], mixed oxides [20], layered double hydroxides [21], and activated carbon [3,22] have been developed. However, the catalysts prepared by polymer graft techniques cannot withstand high temperature. Some of their macroscopic properties, such as specific surface area and porosity, are not as good as with inorganic supports. It is well known that the active components are normally located on the surface of the inorganic supports and easily leach out leading to the deactivation of the catalysts [23]. To achieve the activity and selectivity of the immobilization catalysts being as high as in solution, the immobilization of complexes should be anchored as flexible as possible to the supports. In recent years, organic–inorganic hybrid (OIH) materials, where the organic functionality is covalently attached to porous inorganic solids, have attracted a great deal of attention [24–27]. The goal is to utilize the organic moiety as the active site and the inorganic solid to provide avenues for recovering the active site.

Palladium chloride has been anchored on OIH using 2-pyridine compounds as organic ligand and used as an active

* Corresponding author. Tel.: +86 27 87543732; fax: +86 27 87544532.
E-mail address: ligxabc@163.com (G. Li).



Scheme 1. Preparation of the immobilized palladium catalyst.

catalyst for the carbonylation of phenol in our previous study [28]. However, the synthetic procedure of the supported catalysts is long and fussy. In this work, palladium chloride anchored on functionalized silica modified by 1,2-diaminocyclohexane was prepared using a sol–gel technique, and it was denoted by OIH–DACH–PdCl₂. The synthetic route is shown in Scheme 1. The effects of various reaction parameters such as solvent, inorganic cocatalyst, Pd loading and the molar ratio of phenol to Pd on the catalytic performance of OIH–DACH–PdCl₂ were also studied.

2. Experimental

2.1. Synthetic procedures

2.1.1. Preparation of

N,N-bis[(triethoxysilyl)propyl]-1,2-diaminocyclohexane **1**

The secondary amine *N,N*-bis[(triethoxysilyl)propyl]-1,2-diaminocyclohexane **1** was prepared according to the literature [29].

2.1.2. Preparation of the functionalized silica **2**

35 ml ethanol and 55 ml 0.2 M aqueous ammonia were added to the mixture of 18.7 g (90 mmol) tetraethoxysilane (TEOS) and 5.2 g (10 mmol) **1**. The resulting mixture was stirred at room temperature for 4 h to produce the sol. The sol was transferred to a beaker and covered with a filter paper for several days until the gel appeared. The functionalized gel **2** was recovered by filtration, washed thoroughly with distilled water and ethanol, and dried at 60 °C under vacuum.

2.1.3. Preparation of catalyst **3**

Pd(PhCN)₂Cl₂ was prepared according to the literature [30]. 0.766 g (2 mmol) Pd(PhCN)₂Cl₂, 2 g OIH **2** and 100 ml CH₂Cl₂ were placed in a round-bottom flask, stirred at room temperature for 24 h, filtered and washed. The product was Soxhlet-extracted with CH₂Cl₂ for 24 h to remove Pd(PhCN)₂Cl₂ physically adsorbed, and dried at room temperature under vacuum to achieve the catalyst OIH–DACH–PdCl₂ **3**. The Pd loading was 5.1 wt.% which was determined by atom absorption (AA). Other catalysts with different Pd loadings were synthesized according to the above-mentioned synthetic process, with the amount of OIH **2** changed.

2.2. Catalytic reaction

OIH–DACH–PdCl₂ (containing Pd 0.04 mmol), inorganic cocatalyst (containing inorganic ions 0.24 mmol), 1.2 mmol benzoquinone (BQ), 1.2 mmol tetrabutylammonium bromide (TBAB), 40 mmol phenol, 3.3 g 3 Å molecular sieves (M.S.) and 20 ml tetrahydrofuran (THF) were charged into a 100 ml stainless steel autoclave. After the reactor was purged with O₂ three times, 0.4 MPa O₂ and 4 MPa CO were charged successively. The reaction mixture was kept at 110 °C for 5 h, then cooled to room temperature and vented. The products were analysed by GC after removing the catalysts **3**, and the yield of DPC was calculated based on the charged phenol.

2.3. Reuse of the recovered catalyst

The catalyst OIH–DACH–PdCl₂ was recovered and reused by the following steps: the reaction mixture was cooled to room temperature, and filtered. The solid catalyst was washed with CH₂Cl₂ after filtration, dried at 80 °C under vacuum, and then reused in the next run without changing the reaction conditions.

2.4. Determination of Pd leaching

To determine the Pd content in the solution, part of the filtrate after removing the solvent was placed in a 50 ml crucible, heated to 600 °C at a heating rate of 10 °C/min, and then calcined at 600 °C for 3 h. The residue was dissolved in 20 ml aqua regia and diluted to 50 ml. The Pd leaching in solution was determined by AA.

2.5. Apparatus

Infrared spectroscopy (IR) was carried out using an EQUINOX 55 spectrometer in the range of 4000–500 cm⁻¹. The solid samples were ground with dried KBr powder, and compressed into a disc prior to analysis. X-ray photoelectron spectra (XPS) were recorded on a Kratos XSAM800 spectrometer with Mg Kα radiation (1253.6 eV) operated at 12 kV and 10 mA without a monochromator. The thermal property was observed by thermogravimetric analyses with a Perkin-Elmer TG-DTA 7 spectrometer under argon at a heating rate of 10 °C/min. The

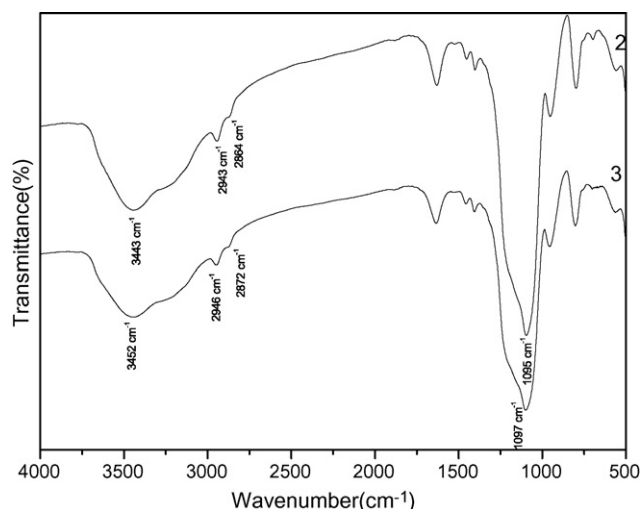


Fig. 1. IR spectra of functionalized silica **2** and catalyst **3**.

Pd loading and leaching in solution were determined by AA with a Perkin-Elmer Analyst 300 using acetylene (C_2H_2) flame. The analysis of the reaction products was performed using an Agilent GC-1790 gas chromatograph with HP-5 capillary column ($30\text{ m} \times 0.32\text{ mm} \times 0.25\text{ }\mu\text{m}$, 5% phenyl methyl-siloxane) and FID detector. GC-MS were obtained on a Finnigan Trace mass spectrometer (70 eV EI). X-ray diffraction (XRD) measurements were taken on a χ 'Pert PRO with Cu $K\alpha$ radiation in the range of $2\theta = 10\text{--}80^\circ$.

3. Results and discussion

3.1. Characterization

3.1.1. IR

The IR spectra of functionalized silica **2** and catalyst **3** are shown in Fig. 1. The bands at 3443 and 1095 cm^{-1} in the IR spectrum of support **2** are assigned to the symmetric stretching vibration of isolated Si–OH and Si–O–Si in tetramer, respectively. These results reveal the formation of a SiO_2 net structure in support **2**. The peaks of the organic groups are relative weak because of their low content in functionalized silica. The weak bands at 2943 and 2864 cm^{-1} are assigned to asymmetric and symmetric stretching vibrations of $-CH_2$ units, respectively. All characteristic peaks exist but give a small shift in the spectrum of catalyst **3** compared with support **2**. This is probably due to the fact that the chemical environment has been changed for the Pd(II) combine covalently to the support **2**.

3.1.2. XPS

The XPS of the support and catalyst are shown in Fig. 2. The N atoms in the support donate electron to Pd(II): as a result, the electron cloud around Pd(II) increases and the peak of Pd $3d_{5/2}$ at 337.0 eV in OIH–DACH–PdCl $_2$ is lower than that of PdCl $_2$ at 337.9 eV [31]. The peak of N1s in OIH–DACH–PdCl $_2$ at 400.1 eV is higher than that of OIH at 399.5 eV . These changes of binding energies reveal that there is an electronic interac-

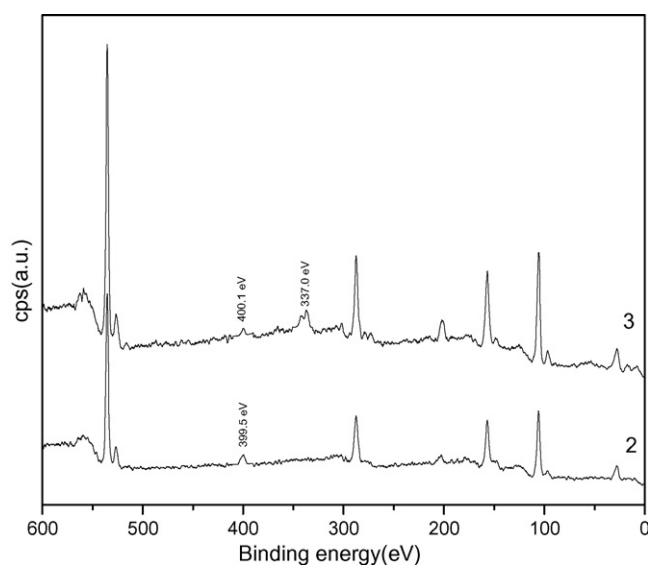


Fig. 2. XPS of support **2** and catalyst **3**.

tion between Pd(II) and N, which indicates the formation of immobilized catalyst **3**.

3.1.3. TG-DTA

The TG and DTA curves of OIH–DACH–PdCl $_2$ **3** are given in Fig. 3. The TG curve shows that the weight loss of catalyst **3** takes place in three steps. Continuous weight loss is observed below 100°C corresponding to the release of water physically adsorbed on the surface of the catalyst. During this step, 1.4% water is removed. In the range of $210\text{--}380^\circ\text{C}$, the strong endothermic peak at 268.3°C accompanies major weight loss of 14%, which is due to the thermal degradation of the organic moieties. Loss of water related to removal of the residual $-OH$ groups of sol-gel inorganic matrix occurs in the range of $400\text{--}600^\circ\text{C}$. The total weight loss amounts to 20.6%, and so the weight of residue is 79.4%, which is ascribed to the SiO_2 and palladium chloride in the catalyst. The result of TG-DTA reveals that the organic moieties have been combined to the inorganic support. This is consistent with the IR analysis.

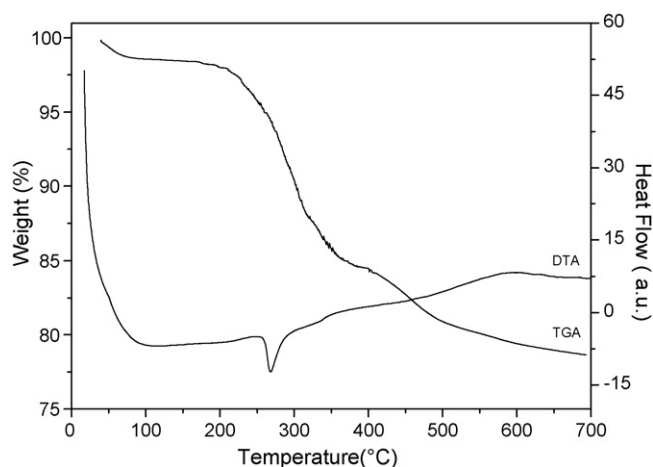


Fig. 3. TGA-DTA curves of catalyst **3**.

Table 1
Catalytic activity of homogeneous catalyst and heterogeneous catalyst^a

Entry	Catalysts	Pd loading (wt.%)	Y_{DPC} (%)	TON (mol DPC/mol Pd)	Pd loss (wt.%) ^c
1	PdCl ₂	–	6.2	31.0	–
2	Pd(OAc) ₂	–	9.2	46.0	–
3	PdCl ₂ /2,2'-bipyridyl [13]	–	0.15	–	–
4	PdCl ₂ /1,10-phenatrolone [13]	–	0.65	–	–
5	PdCl ₂ /1,10-phenatrolone	–	0.8	4	–
6	PdCl ₂ /1,2-diaminocyclohexane	–	0.7	3.5	–
7	OIH–DACH–PdCl ₂	5.1	12.0	60.0	3.0
8	OIH–DACH–Pd(OAc) ₂ ^b	4.2	12.9	64.5	5.2

^a Reaction conditions: $n(\text{Pd}^{2+}):n(\text{Cu}^+):n(\text{BQ}):n(\text{Bu}_4\text{NBr}):n(\text{PhOH}) = 1:6:30:30:1000$, reaction temperature 110 °C, reaction time 5 h.

^b OIH–DACH–Pd(OAc)₂ was synthesized according to the synthetic process of OIH–DACH–PdCl₂.

^c Pd in solution/total amount of Pd introduced.

3.2. Catalytic activity

3.2.1. Activity comparison of homogeneous and heterogeneous catalysts

It is well known that palladium salts such as palladium acetate and palladium chloride are able to catalyze the carbonylation of phenol to produce DPC [12]. Although the aim of immobilization is to solve the problems of homogeneous catalyst such as separation and regeneration, heterogenized palladium complex will be insignificant if the catalytic activity is low. The activity comparison of homogeneous and heterogeneous catalysts are shown in Table 1. It is well known that Pd(OAc)₂ is a weakly coordinated palladium salt and that the chloride ligand in PdCl₂ is a comparatively strong electron-withdrawing ligand [32]. So OAc[–] will be replaced very rapidly with PhO[–] and CO to produce intermediate PhO–Pd–CO–OPh in the oxidative carbonylation, producing DPC by reductive elimination. As a result, Pd(OAc)₂ showed higher catalytic activity compared with PdCl₂ in the homogeneous system (entries 1–2).

Palladium complexes can be used as the main catalyst in the oxidative carbonylation of phenol to DPC except for simple palladium salts [1,13]. The electron donor ability and size of ligands are important factors in determining the stability of complexes [33]. The reductive elimination rate in the oxidative carbonylation was accelerated by bulky substituents of ligands for steric repulsion [1]. Table 1 shows that the catalytic activity of 2,2'-bipyridyl and 1,10-phenatrolone without substituents was very low (entries 3–5). Although the catalytic activity was improved by the presence of bulky substituents and electron donor groups, the procedure for introducing substituents to the ligands was very fussy and the catalytic active species cannot be recovered [1,13,34].

Compounds, which contain active organic moieties such as –NH₂, –CO– and –CHO are often selected as organic ligands [16,24] during the synthesis of OIH support by the sol–gel approach. These active organic moieties reacted with silane coupling agents to form hydrolysis precursors. 1,2-diaminocyclohexane showed similar catalytic activity in the reaction compared with 2,2'-bipyridyl and 1,10-phenatrolone in homogeneous catalytic system (entries 5 and 6). So 1,2-diaminocyclohexane was selected because of the amine group included and the commercial availability.

Although 1,2-diaminocyclohexane revealed poor activity in the homogeneous catalytic system, the catalytic activity was improved greatly in the heterogeneous catalytic system. For example, the yield of DPC was 0.7% when 1,2-diaminocyclohexane was used as ligand in the homogeneous system (entry 6), and the yield of DPC increased sharply to 12.0% when the reaction was catalyzed by OIH–DACH–PdCl₂ (entry 7). This positive effect is probably due to the –(CH₂)₃– group in the silane coupling agent and SiO₂ net structure on which secondary amine was anchored; the SiO₂ net structure maybe play the role of a bulky substituent. So the cleavage rate of Pd–C in the intermediate produced during the reaction was accelerated because of high steric hindrance of supported catalyst [13]. Both steric hindrance and electronic donor ability improved the catalytic activity of the heterogeneous catalyst significantly, so the activity of OIH–DACH–PdCl₂ and OIH–DACH–Pd(OAc)₂ was almost equivalent and was higher than that of the homogeneous system. Table 1 shows that OIH–DACH–PdCl₂ revealed excellent catalytic activity as the yield of DPC reached up to 12.0% (entry 7), which was close to 12.9% for OIH–DACH–Pd(OAc)₂ (entry 8); the Pd loss was only 3.0%.

3.2.2. The choice of inorganic cocatalyst and solvent

The inorganic/organic cocatalysts are generally added to the reaction system of the oxidative carbonylation of phenol. Acetate salts such as Co(OAc)₂, Mn(OAc)₂ and Cu(OAc)₂ are effective inorganic cocatalysts, and CH₂Cl₂ is often selected as the solvent in the homogeneous system. However, our study has shown that the Pd leaching was relatively high in the PdCl₂–OIH–Co(OAc)₂–CH₂Cl₂ heterogeneous reaction system, in which the catalyst was anchored with 2-pyridine species [28]. So the effects of the inorganic cocatalyst and solvent on the yield of DPC and Pd leaching were studied here. The data in Table 2 show that similar results were observed for the catalyst prepared from 1,2-diaminocyclohexane in the presence of acetate salts and CH₂Cl₂. The results suggest that Pd leaching was relevant to solvents and cocatalyst anions. Since the solution contained a large amount of acetate anions in the presence of acetate salts, these anions may form ion pairs with Pd(II). Complexation of Pd(II) by acetate anions is a sufficient driving force to bring Pd(II)

Table 2
Effect of the inorganic cocatalyst and solvent on the oxidative carbonylation of phenol^a

Entry	Inorganic cocatalyst	Solvent	Y_{DPC} (%)	TON (mol DPC/mol Pd)	Pd loss (wt.%) ^b
1	Mn(OAc) ₂	CH ₂ Cl ₂	6.2	31.0	8.9
2	Co(OAc) ₂	CH ₂ Cl ₂	5.9	29.5	9.1
3	Cu(OAc) ₂	CH ₂ Cl ₂	5.2	26.0	9.3
4	Cu ₂ O	CH ₂ Cl ₂	5.6	28.0	5.8
5	Mn(OAc) ₂	THF	10.9	54.5	6.2
6	Co(OAc) ₂	THF	9.4	47.0	5.6
7	Cu(OAc) ₂	THF	9.3	46.5	6.1
8	Cu ₂ O	THF	12.0	60.0	3.0

^a Reaction conditions: $n(\text{Pd}^{2+}):n(\text{inorganic cocatalyst}):n(\text{BQ}):n(\text{Bu}_4\text{NBr}):n(\text{PhOH}) = 1:6:30:30:1000$, reaction temperature 110 °C, reaction time 5 h, Pd loading = 5.1 wt.%.

^b Pd in solution/total amount of Pd introduced.

into the solution [19]. Pd leaching reached up to 9.3% in OIH–DACH–PdCl₂–Cu(OAc)₂–CH₂Cl₂ system (entry 3), but there was only 3.0% Pd loss in OIH–DACH–PdCl₂–Cu₂O–THF system with a DPC yield as high as 12.0% (entry 8).

There are some byproducts formed during the oxidative carbonylation of phenol to DPC, but the main byproducts changed with different catalytic systems. Goyal et al. [6] reported that *o*-phenylene carbonate was the main byproduct, Ishii et al. [14] pointed out that phenyl salicylate was the main side product, and Xue et al. [23] mentioned that *p*-benzoquinone, phenyl acetate and tributylamine were the main products. In the present work, the products of both the OIH–DACH–PdCl₂–Co(OAc)₂–CH₂Cl₂ system and the OIH–DACH–PdCl₂–Cu₂O–THF system were analyzed by GC–MS. Phenyl salicylate, tributylamine, *p*-bromophenols and phenyl acetate were detected in the OIH–DACH–PdCl₂–Co(OAc)₂–CH₂Cl₂ catalytic system, and phenyl salicylate was the main byproduct. However, no phenyl acetate was detected in the OIH–DACH–PdCl₂–Cu₂O–THF catalytic system. These results suggest that the acetate anion in phenyl acetate came from the acetate salt charged into the reaction system and the distribution of species in products was related to the inorganic cocatalyst.

In summary, the OIH–DACH–PdCl₂–Cu₂O–THF catalytic system not only showed excellent activity and lower Pd leaching but also produced fewer byproducts.

3.2.3. Effect of Pd loading

Heterogenized catalysts with different Pd loadings were prepared to investigate the effect of Pd loading on the oxidative carbonylation of phenol. Table 3 presents the results as the Pd

loading varied from 3.6 to 8.6 wt.%. The Pd loading showed a significant effect on the yield of DPC and Pd leaching. The yield of DPC increased with increasing Pd loading at low Pd contents. This is attributed to the increase in the number of catalytic active sites with increasing loading. The maximum 12.0% yield of DPC was observed at 5.1 wt.% Pd loading. Since the aggregation of Pd led to the dispersion of active sites to decrease at Pd contents above 5.1 wt.%, the catalytic activity decreased and the yield of DPC decreased consequently. In addition, the Pd leaching increased with increasing Pd loading, and the highest 6.0% Pd leaching was observed at 8.6 wt.% loading.

3.2.4. Effect of the molar ratio of phenol to Pd

The effect of the molar ratio of phenol to Pd on the reaction with the same amount of palladium is shown in Table 4. The yield of DPC decreased from 11.6% (entry 1) to 2.5% (entry 6) with increasing molar ratio of phenol to Pd from 500 to 4000, and TON increased from 29 to 50. However, the trend in the increase in TON became smaller at higher molar ratios. It is interesting that TON remained almost unchanged when the molar ratio of phenol to Pd was beyond 1000. This is possibly due to the catalytic active sites being employed entirely with increasing amount of phenol. These results indicate that each active site exhibited almost equivalent catalytic activity, and that the amount of DPC produced during the reaction was almost unchanged when the amount of palladium was kept constant at higher molar ratios.

3.2.5. Pd state in the recovered catalyst

Hatanaka et al. [4] have proposed that the possible mechanism of oxidative carbonylation of phenol to DPC is a “multi-step

Table 3
Effect of Pd loading on the oxidative carbonylation of phenol^a

Entry	Pd loading (wt.%)	Y_{DPC} (%)	TON (mol DPC/mol Pd)	Pd loss (wt.%) ^b
1	3.6	7.3	36.5	1.9
2	4.4	9.1	45.5	2.8
3	5.1	12.0	60.0	3.0
4	6.8	10.9	54.5	4.4
5	8.6	9.4	47.0	6.0

^a Reaction conditions: $n(\text{Pd}^{2+}):n(\text{Cu}^+):n(\text{BQ}):n(\text{Bu}_4\text{NBr}):n(\text{PhOH}) = 1:6:30:30:1000$, reaction temperature 110 °C, reaction time 5 h.

^b Pd in solution/total amount of Pd introduced.

Table 4
Effect of the phenol/Pd molar ratio on the oxidative carbonylation of phenol^a

Entry	Phenol/Pd (molar ratio)	Y_{DPC} (%)	TON (mol DPC/mol Pd)	Pd loss (wt.%) ^b
1	500	11.6	29.0	5.3
2	667	10.8	36.0	4.9
3	1000	9.3	46.5	5.0
4	2000	4.7	47.0	4.4
5	3000	3.2	48.0	5.2
6	4000	2.5	50.0	5.0

^a Reaction conditions: $n(\text{Pd}^{2+}):n(\text{Cu}^+):n(\text{BQ}):n(\text{Bu}_4\text{NBr}) = 1:6:30:30$, reaction temperature 110 °C, reaction time 5 h, Pd loading = 8.6 wt.%.

^b Pd in solution/total amount of Pd introduced.

Table 5
Catalytic activity of fresh catalyst and recovered catalyst^a

Entry	Catalyst	Y_{DPC} (%)	TON (mol DPC/mol Pd)	Pd loss (wt.%) ^d
1	Fresh	3.3	16.5	3.8
2	Recovered ^b	3.1	15.5	3.6
3	Recovered ^c	0.5	2.5	2.8

^a Reaction conditions: $n(\text{Pd}^{2+}):n(\text{Cu}^+):n(\text{BQ}):n(\text{Bu}_4\text{NBr}) = 1:6:30:30$, reaction temperature 110 °C, reaction time 5 h, Pd loading = 5.1 wt.%, 3 Å M.S. was not used.

^b Second run.

^c Inorganic/organic cocatalysts were not used, second run.

^d Pd in solution/total amount of Pd introduced.

electron transfer” catalytic cycle in which the chemical state of palladium changed between Pd(II) and Pd(0). In addition, it has been confirmed that water can react with DPC to produce phenol and CO₂ [2,34]. In order to improve the yield of DPC, 3 Å M.S. was added to remove water formed during the reaction. However, as 3 Å M.S. is crushed easily by the stirring during the reaction, it is difficult to separate and recover the heterogeneous catalyst. Therefore, the catalytic performance of OIH–DACH–PdCl₂ was studied without employing a dehydrating agent to investigate the state of palladium in the recovered catalyst. The XRD patterns of the fresh catalyst and the recovered catalyst after one run without redox cocatalyst are shown in Fig. 4. The weak and wide peaks at $2\theta = 22.86^\circ$ and 23.10° in the curves are ascribed to the amorphous structure of the support. X-ray diffraction curve of the recovered catalyst (curve b in Fig. 4) exhibits three characteristic peaks at $2\theta = 40.21^\circ$, 46.90° and 68.21° , which confirms the existence of Pd(0) (JCPDS 01-1201, 05-0681) in the catalytic cycle. The size of the Pd(0) particles is 20.8 nm which

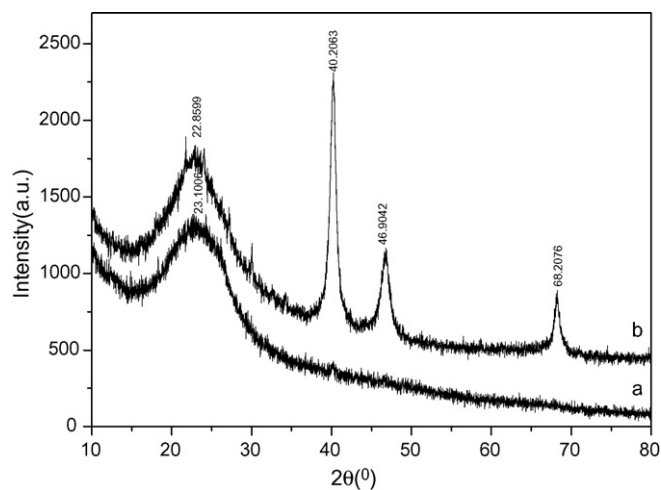
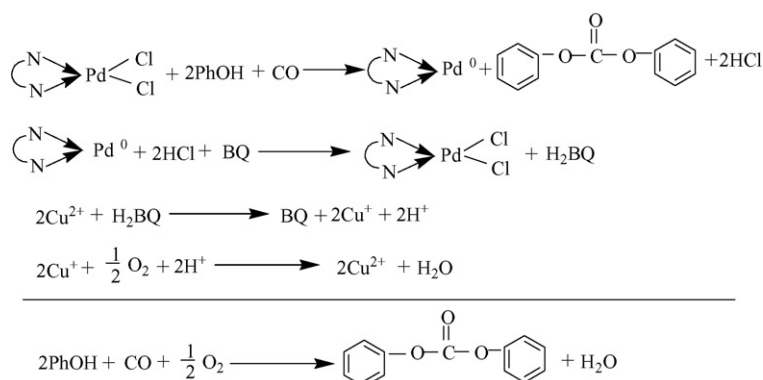


Fig. 4. XRD patterns of catalysts (a) fresh catalyst (Pd loading = 5.1 wt.%); (b) recovered catalyst (after one run).



Scheme 2. A possible mechanism for the oxidative carbonylation of phenol to DPC over heterogeneous catalyst.

was estimated by Scherrer equation [35]. The result indicates that large metal particles formed in the recovered catalysts due to the aggregation of Pd(0) particles.

The catalytic activity of supported catalyst without using dehydrating agent is shown in Table 5. The yield of DPC only slightly changed from 3.3% to 3.1% during the reuse of heterogeneous catalyst in the presence of redox cocatalysts. However, the recovered catalyst showed poor catalytic activity without redox cocatalysts; the yield of DPC decreased drastically from 3.3% to 0.5%. It is known that Pd(0) is inactive in the reaction [12], so Pd(0) must be transformed to Pd(II) by the cocatalyst during the reaction to keep the catalytic activity. It is reasonable to suppose that the recovered catalyst may be a mixture of Pd(II) and Pd(0) from the results of Table 5 and Fig. 4, which caused a change in the colour of the catalyst from gray to black. Thus, the oxidative carbonylation of phenol to DPC follows the well-known “multi-step electron transfer mechanism”. A possible mechanism in the presence of Cu₂O is proposed in Scheme 2.

4. Conclusions

OIH–DACH–PdCl₂ catalysts anchored on functionalized silica were prepared by the sol–gel technique using CPTES as silane coupling agent, 1,2-diaminocyclohexane as ligand and TEOS as hydrolysis precursor. The catalytic activity of the heterogeneous catalyst was also studied in the oxidative carbonylation of phenol to DPC. Cu₂O and THF were found to be the best combination with the heterogeneous catalyst in terms of higher yield of DPC, lower Pd leaching in solution, and fewer byproducts. OIH–DACH–PdCl₂ revealed more excellent catalytic performance compared with the homogeneous catalyst as the yield of DPC reached 12.0% with TON = 60 mol DPC/mol Pd in the presence of Cu₂O and THF. The Pd loading affected the oxidative carbonylation significantly and the optimum Pd loading was 5.1 wt.%. The existence of Pd(0) in the catalytic cycle was verified by XRD, and the state of palladium in the recovered catalyst was a mixture of Pd(II) and Pd(0). A possible mechanism for the reaction in the presence of Cu₂O was also proposed.

Acknowledgements

This work was supported financially by 863 Program of the Ministry of Science and Technology of China (2004AA32G030). We would like to thank The Centre of Analysis and Measurement, Wuhan University for the XPS analyses.

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