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Oxidative carbonylation of phenol to diphenyl carbonate catalyzed by palladium complexes bridged with *N,N*-ligands over functionalized silica

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Heterogeneous palladium catalysts anchored on functionalized silica were prepared by sol–gel methods and their catalytic properties for the oxidative carbonylation of phenol to diphenyl carbonate (DPC) were investigated. The catalysts were characterized by means of IR, XPS, EA and BET. The Pd loading in the heterogeneous catalysts and leaching in solution were detected by atomic absorption. The effects of different reaction parameters such as temperature, solvent and inorganic cocatalyst on the yield of DPC and Pd leaching were also studied. It was found that Cu_2O and tetrahydrofuran (THF) were the best partners with these heterogeneous catalysts. In the presence of 3 Å molecular sieves as dehydrating agent, the heterogeneous palladium catalyst prepared from 2-acylpyridine revealed excellent catalytic performance and stability at 110 °C for 5 h, giving 13.7% yield of DPC based on phenol and 4.0% Pd loss in solution. The heterogeneous catalyst was more active and stable compared with traditional supported Pd–C catalyst under the same reaction conditions. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: organic–inorganic hybrid; sol–gel; heterogeneous catalyst; phenol; oxidative carbonylation; diphenyl carbonate

INTRODUCTION

Heterogeneous catalysts in a gas–liquid–solid system provide numerous opportunities for recovering and recycling the catalysts from the reaction mixture. These features can lead to improved processing steps, better process economics and environmentally friendly industrial manufacture. In recent years, the development of such catalysts has attracted significant interest. These heterogeneous catalysts have been prepared using a range of supports from inorganic solids to glass tubing; however, some of these supported catalysts generally suffer from diffusion limitations and dissolution under the reaction conditions.[1] Since much is known about how organic moieties can serve as catalysts for homogeneous reactions, the immobilization of these entities onto solids to create organic–inorganic hybrid (OIH) catalysts, where the organic functionality is covalently attached to porous inorganic solids, can be accomplished with some aspects of design. The goal is to utilize the organic moiety as the active site and the inorganic solid to provide avenues for recovery and possible recycling of the organic active site.[2]

Diphenyl carbonate (DPC), an important precursor of polycarbonate, is conventionally synthesized from phosgene and phenol. In recent years, the need has arisen for a method that does not require the use of highly toxic phosgene because of increasing demands for a safer and environmentally benign process for DPC synthesis.[3] Several alternative methods have been developed or proposed.[4,5] Among them, the one-step oxidative carbonylation of phenol with carbon monoxide and oxygen to DPC has attracted great interest and is considered as one of the best routes to prepare DPC without employing toxic phosgene, and H_2O is the sole byproduct.[6] However, direct oxidative carbonylation of phenol to DPC has usually been catalyzed by Pd complexes and inorganic/organic cocatalysts following the well-known 'redox' or 'multi-step electron transfer mechanism',[7–12] and 3 Å molecular sieves (MS) are employed as a dehydrating agent to remove water produced during the reaction.[13–15]

To facilitate recovery of the noble palladium catalyst in homogeneous reactions, heterogenized Pd complexes

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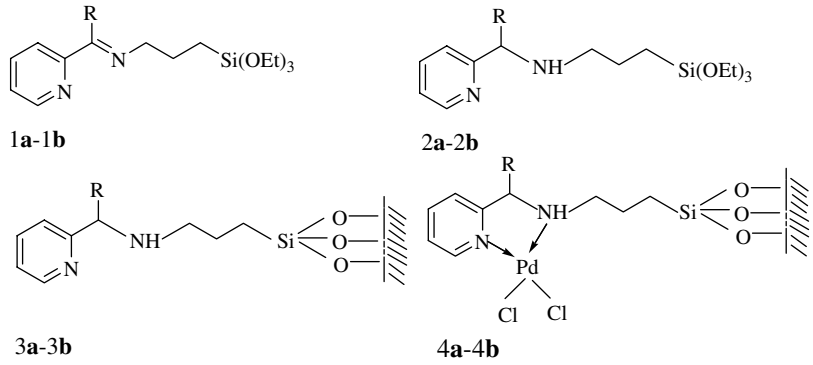

Scheme 1. Structure of intermediates and palladium complex.

on supports such as polymer,[16] SiO_2,[4] zeolites,[17] mixed oxides,[18] double-layered hydroxides[19] and supported metallic palladium on activated carbon[4,20,21] have been developed. However, the catalysts prepared by polymer graft techniques cannot bear high temperatures. Some of their macroscopic properties, such as specific surface areas and porosity, are not as good as 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 heterogeneous catalysts.[22] In the present work, Schiff bases **1a** and **1b** were synthesized from compounds containing N ligands, then reduced by $NaBH_4$ to make secondary amines **2a** and **2b**. OIH **3a** and **3b** were prepared using the sol–gel approach using γ-aminopropyltriethoxysilane (APTES) as the silane coupling agent and tetraethoxysilane (TEOS) as the precursor, then reacted with $PdCl_2(PhCN)_2$ to achieve heterogeneous catalysts $PdCl_2$–OIH **4a** and **4b**. The influence of various reaction parameters on the catalytic performance of $PdCl_2$–OIH for the synthesis of DPC by oxidative carbonylation was studied in this paper.

EXPERIMENTAL

Materials

All solvents were distilled prior to use. 2-Pyridinecarboxaldehyde and 2-acetylpyridine were supplied from Aldrich and used as received. Other reagents were analytical grade and used without further purification.

Apparatus

Infrared spectroscopy (IR) was recorded on an Equinox 55 spectrometer in the range 4000–500 cm^{-1}. The solid samples were ground with dried potassium bromide (KBr) powder, and compressed into a disc prior to analysis.

X-ray photoelectron spectra (XPS) were recorded on a Kratos XSAM800 spectrometer with Mg K_α radiation (1253.6 eV) operated at 12 kV and 10 mA without a monochromator. The pressure inside the analytical chamber was 2×10^{-7} Pa. C, H and N elemental analysis (EA) was carried out on Vario elementer.

The specific surface area of OIH was determined by nitrogen adsorption–desorption isotherm at 77.35 K using the one-point modified BET method on a Gemini 2360 analyzer.

The Pd loading and leaching in solution were detected by atomic absorption (AA) with a PerkinElemer Analyst 300 using acetylene (C_2H_2) flame and graphite stove. The analysis of the reaction products was performed using an Agilent GC-1790 gas chromatograph with HP-5 capillary column (30 m × 0.32 mm × 0.25 μm, 5% phenyl methyl-siloxane) and FID detector.

Preparation of catalyst

The catalysts were synthesized according to the literature.[23] Schiff base **1a** (**1b**) was prepared as follows: 1.07 g (10 mmol) 2-pyridinecarboxaldehyde (1.21 g 2-acetylpyridine) was reacted with 2.43 g (11 mmol) APTES in 30 ml ethanol over 4 g 3 Å MS in reflux. The complete conversion of 2-pyridinecarboxaldehyde (2-acetylpyridine) was monitored by TLC using hexane : ethanol = 6 : 1 (v/v) as mobile phase; then the reaction mixture was cooled to room temperature, and dried at 100 °C under vacuum after removing the solvent.

Methanol solution, 20 ml, of 0.76 g (20 mmol) $NaBH_4$ was added slowly to a magnetically stirred 20 ml methanol solution of 3.1 g (10 mmol) **1a** (3.24 g **1b**), then the resulting solution was refluxed until the complete conversion of **1a** (**1b**) monitored with TLC using hexane : ethanol = 4 : 1 (v/v) as mobile phase (ca. 4–5 h); 40 ml water was added to eliminate the excessive $NaBH_4$. After extraction with CH_2Cl_2, the product **2a** (**2b**) was dried at 100 °C under vacuum after removing the solvents.

Ethanol, 35 ml, and 55 ml 0.2 M aqueous ammonia were added to the mixture of 18.72 g (90 mmol) TEOS and 3.12 g (10 mmol) **2a** (3.26 g **2b**), then stirred at room temperature for 4 h to produce a sol. The sol was transferred to a beaker and covered with filter paper for several days until the

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gel appeared. The functionalized gel **3a** (**3b**) was recovered by filtration, washed thoroughly with distilled water and ethanol, then dried at 60 °C under vacuum.

The $PdCl_2(PhCN)_2$ complex was prepared according to the reported procedure;[24] 0.885 g (5 mmol) $PdCl_2$ was dissolved in 10 ml benzonitrile at 100 °C, then stirred for 4 h. The solution was cooled in an ice-bath to precipitate the product, filtered and dried at 60 °C under vacuum. $PdCl_2(PhCN)_2$, OIH and CH_2Cl_2 were placed in a round flask, stirred at room temperature for 24 h, filtered and washed, Soxhlet-extracted with CH_2Cl_2 for 24 h and dried at room temperature under vacuum to achieve the supported catalyst **4a** (**4b**).

Catalytic reaction

A typical activity test procedure is as follows: $PdCl_2$–OIH (containing Pd 0.04 mmol), 0.24 mmol inorganic cocatalyst, 129.6 mg (1.2 mmol) benzoquinone (BQ), 386.4 mg (1.2 mmol) tetrabutylammonium bromide (Bu_4NBr), 3.76 g (40 mmol) phenol, 3.3 g 3 Å MS and 20 ml solvent were charged into a 100 ml stainless autoclave. After the reactor was purged with O_2 three times, 0.4 MPa O_2 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, and the yield of DPC was calculated based on the charged phenol.[25]

Reuse of recovered catalyst

The supported catalyst $PdCl_2$–OIH was recovered and reused by the following steps: the reaction mixture was cooled to room temperature, the solid catalyst was washed with CH_2Cl_2 after filtration, dried at 80 °C under vacuum, then reused in the next run without changing the reaction conditions.

Determination of Pd leaching

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

RESULTS AND DISCUSSION

The catalysts were characterized by means of IR, XPS, EA and BET, and the results are given in this section. The influence of various reaction parameters such as solvent, inorganic cocatalyst, reaction temperature and organic moieties on the catalytic performance, the recycle catalytic performance of $PdCl_2$–OIH and active comparison of $PdCl_2$–OIH and the traditional supported catalyst Pd–C are also discussed here.

Characterization

The IR spectra of Schiff base **1b,** secondary amine **2b** and OIH **3b** are shown in Fig. 1. The bands at 3060 and 3056 cm^{-1} in the spectra of **1b** and **2b** are assigned to C–H asymmetric stretching vibrations of the pyridine ring. The peaks at 2968, 2928 and 2882 cm^{-1} are due to asymmetric stretching vibration of $-CH_3$ units, and asymmetric and

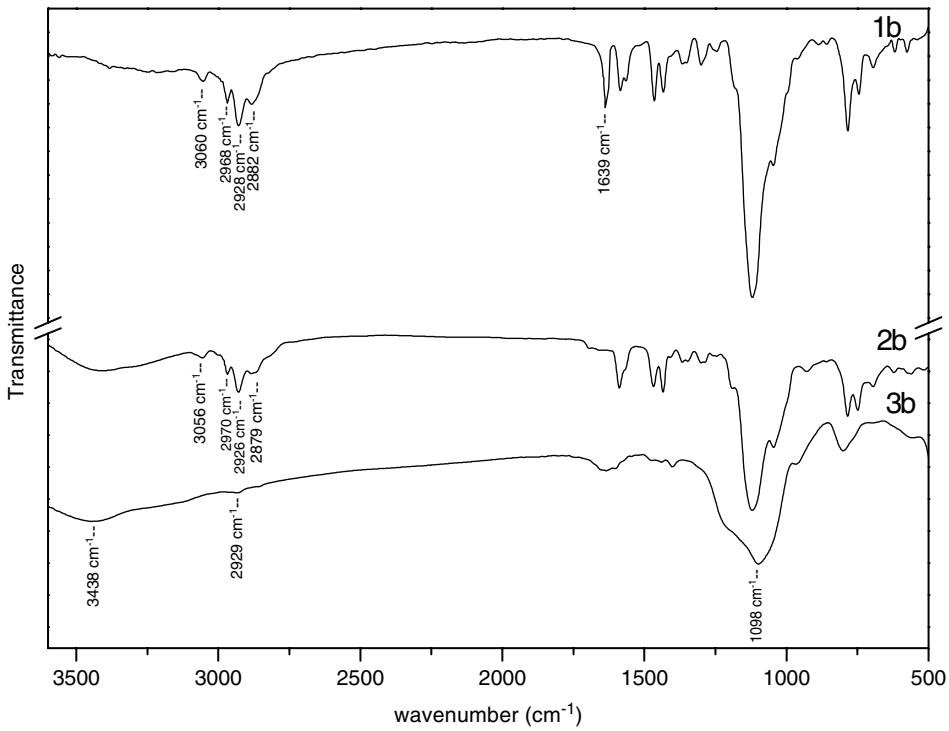

Figure 1. IR spectra of Schiff base **1b,** secondary amine **2b** and support **3b**.

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Table 1. EA and BET analysis of support **3b**

	EA[a]				BET
Sample	C (%)	H (%)	N (%)	C : N ratio	Surface area, m^2/g
Support **3b**	16.16 (15.89)	2.56 (1.99)	3.69(3.71)	4.37(4.29)	204.8

[a] Theoretical values in brackets.

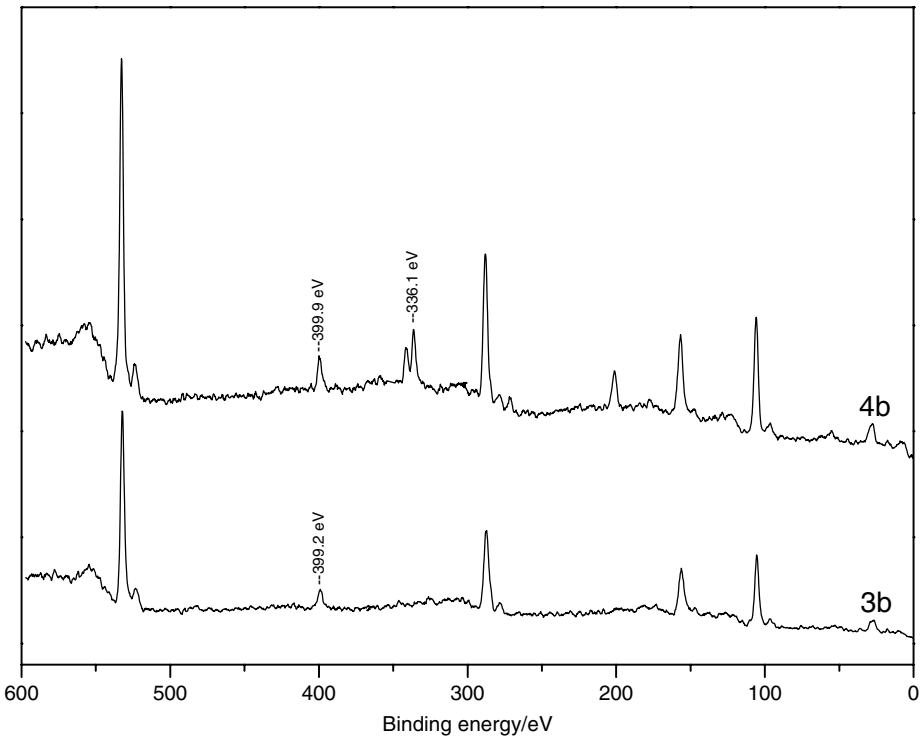

Figure 2. XPS of support **3b** and heterogeneous catalyst **4b**.

symmetric stretching vibrations of $-CH_2$ units, respectively. The significant peak appearing at 1639 cm^{-1} in the spectrum of **1b** is characteristic of the stretching vibrations of C═N in Schiff base compounds. This band is absent in the spectrum of **2b**, indicating that the Schiff base has been reduced by $NaBH_4$ to a secondary amine. In the spectrum of OIH **3b**, bands at 3438 and 1098 cm^{-1} are assigned to isolated ν_{Si-OH} and the symmetric $\nu_{Si-O-Si}$, respectively. These reveal the formation of a SiO_2 net structure in OIH. The molar ratio of the secondary amine **2b** to TEOS is only 1 : 9, so the peaks of the organic groups in the spectrum **3b** are weak. The weak band at 2929 cm^{-1} is assigned to asymmetric ν_{C-H} of $-CH_2$ units.

XPS basically measures the electron binding energy, which is sensitive to the chemical environment of the atom. Any processes, therefore, that involve electron transfer can be detected by XPS. We can determine whether a net transfer of electrons occurred by comparing the change in electron binding energy. Figure 2 presents the XPS of support **3b** and heterogeneous catalyst **4b.** The peak of Pd $3d_{5/2}$ at 336.1 eV in $PdCl_2$–OIH is lower than that of $PdCl_2$ at 337.9 eV,[26] and the peak of N 1s in $PdCl_2$–OIH at 399.9 eV was higher than that of OIH at 399.2 eV. These changes of binding energies indicate that there is an electronic interaction between Pd (II) and N atoms and the formation of immobilized catalyst.

The elemental analysis and BET results of the functionalized silica gel support **3b** are shown in Table 1. The results reveal that the C and N contents correspond well to their theoretical values, but H exhibits a higher value ascribed to some excessive –OH groups of the sol–gel inorganic matrix after reaction. The surface area of OIH support is 204.8 m^2/g, which is close to the results in literature.[23]

Influence of reaction parameters

It is well known that palladium compounds such as palladium acetate and palladium chloride are able to promote the direct oxidative carbonylation of phenol to produce DPC.[21] $Co(OAc)_2$ and CH_2Cl_2 are selected as inorganic cocatalyst and solvent respectively in the homogeneous catalytic system. Since the use of supported Pd catalysts is motivated by the

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ease of catalyst separation and reuse, Pd leaching is one of the most important issues. The aim of the present investigation is to improve the yield of DPC and minimize the Pd content in solution at the end of reaction systems to allow as complete as possible a separation of the noble metal from the reaction mixture. Therefore, the effects of various reaction parameters on the yield of DPC and Pd leaching were studied.

The yield of DPC increased with increasing temperature, increasing from 3.2% (entry 1) to 5.0% (entry 4) as the temperature increased from 80 to 110 °C in Table 2. In contrast, Pd loss decreased with increasing temperature. This might result from catalytic active species in solution being less stable at higher temperature.[27]

The choice of the solvent also affected the yield of DPC and Pd content in reaction solution. Dichloromethane and tetrahydrofuran (THF) were selected as solvents according to the literatures.[3,21] Pd leaching in CH_2Cl_2 (entries 4 and 10) was higher than that in THF(entries 5 and 11), and is due to higher polarity of CH_2Cl_2. The yield of DPC reached 9.6% and Pd loss was 6.2% in THF (entry 5).

The solution contains a large amount of acetate ions in the presence of acetate salts; these ions may form ion pairs with ionic Pd^{2+}. Complexation of Pd^{2+} by acetate is a sufficient driving force to bring Pd^{2+} into solution,[17] which led to higher Pd leaching in solution. Therefore, higher Pd leaching was observed in the system containing acetate salts (entries 4–7). Entry 7 in Table 2 shows that the Pd leaching reached up to 8.2% in the $PdCl_2$–OIH–$Cu(OAc)_2$–CH_2Cl_2 heterogeneous catalytic system. In order to replace acetate salts with more efficient inorganic cocatalysts, various metal compounds such as CuO, CuCl and Cu_2O were investigated to minimize Pd leaching. The yield of DPC was very low using CuO (entry 8) and CuCl (entry 9) as inorganic cocatalysts. However, the $PdCl_2$–OIH revealed good catalytic activity in the presence of Cu_2O. The yield of DPC reached 6.8% and Pd loss was 5.8% (entry 10).

In summary, the yield of DPC and Pd leaching correlated to the reaction temperature, solvent and inorganic cocatalysts. The higher yield of DPC, 7.8%, and lower Pd leaching, 3.6%, were obtained in the Cu_2O–THF system (entry 11). Although the yield of DPC reached 9.6% in $Co(OAc)_2$–THF system (entry 5), the 6.2% of Pd loss was much higher than that in the Cu_2O–THF system. Therefore, in this work, Cu_2O and THF were selected as inorganic cocatalyst and solvent, respectively.

Table 2. Effect of different reaction conditions on the oxidative carbonylation of phenol to DPC[a]

Entry	Inorganic cocatalyst	T (°C)	Solvent	Y_{DPC} (%)	Pd loss[b] (wt%)
1	$Co(OAc)_2$	80	CH_2Cl_2	3.2	10.5
2	$Co(OAc)_2$	90	CH_2Cl_2	4.0	8.2
3	$Co(OAc)_2$	100	CH_2Cl_2	4.2	8.0
4	$Co(OAc)_2$	110	CH_2Cl_2	5.0	7.5
5	$Co(OAc)_2$	110	THF	9.6	6.2
6	$Mn(OAc)_2$	110	CH_2Cl_2	5.8	7.1
7	$Cu(OAc)_2$	110	CH_2Cl_2	4.6	8.2
8	CuO	110	CH_2Cl_2	3.1	5.8
9	CuCl	110	CH_2Cl_2	1.2	4.5
10	Cu_2O	110	CH_2Cl_2	6.8	5.8
11	Cu_2O	110	THF	7.8	3.6

[a] Reaction conditions: $n(Pd^{2+}) : n(\text{inorganic cocatalyst}) : n(BQ) : n(Bu_4NBr) : n(PhOH) = 1 : 6 : 30 : 30 : 1000$, $t = 5$ h, $PdCl_2$–OIH **4a** as catalyst, Pd loading = 4.2%.
[b] Pd in solution/total amount of Pd introduced.

Influence of organic moieties

Both the Schiff base and the secondary amine reduced from it could be used as ligands. Since $-NH_2$ included in the product of APTES cogelled with TEOS can coordinate with Pd (II) to form complex heterogenous catalyst, the product can also serve directly as a ligand. The effects of different organic moieties on the yield of DPC and Pd loss are shown in Table 3. The catalytic activity was poor without adding any organic moiety and gave a lower DPC yield of 1.6% (entry 1); this might result from a competition oxidation of $-NH_2$ to expend O_2 in the system. In addition, part of the $-NH_2$ is consumed in the oxidation process, leading to Pd leaching of up to 7.3% (entry 1). Ligands substituted with methyl group showed higher catalytic activity. This positive effect is probably due to the increase in electron donor ability of the ligand as well as the steric hindrance of the methyl group.[14] Thus, the catalysts prepared from 2-acetylpyridine showed higher yield of DPC (entries 4 and 5) than those from 2-pyridinecarboxaldehyde (entries 2 and 3). The $\pi-\pi$ configuration system, which presents the strong electron-withdrawing effect,[28] formed in Schiff bases. Thus, the electron donor ability of secondary amines is stronger than that of Schiff bases. As a result, secondary amines gave higher yields of DPC (entries 3 and 5) than Schiff bases (entries 2 and 4).

Recycle catalytic performance

It was confirmed that water can react with DPC to produce phenol and CO_2.[6] In order to improve the yield, 3 Å MS was employed to remove water formed during the reaction. Since 3 Å MS is crushed easily with stirring during the reaction, it is difficult to separate and recover the supported catalyst in the heterogeneous catalytic system. The 3 Å MS was not used to investigate the recycle catalytic performance of the recovered catalyst and the results are reported in Table 4. Although the yield of DPC is relatively low compared with the use of 3 Å MS as a dehydrating agent (entry 5 in Table 4), the heterogeneous catalyst revealed good recycle catalytic performance, and the stability for the yield of DPC remained almost unchanged, the mean yield being 4.2% and the mean Pd loss 2.7% during four recycles.

$PdCl_2$–OIH vs Pd–C catalyst

In the presence of Cu_2O and THF, a comparison between $PdCl_2$–OIH and Pd–C was also studied. The results in Table 5

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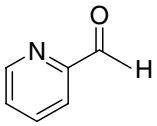
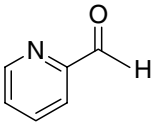
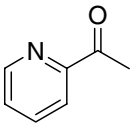
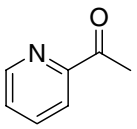
Table 3. Effect of organic moieties on the oxidative carbonylation of phenol to DPC[a]

Entry	Catalysts	Organic moities	Pd loading (wt%)	Y_{DPC} (%)	Pd loss[b] (wt%)
1	$PdCl_2/Si_2O_{3.5}(CH_2)_3NH_2$	—	5.2	1.6	7.3
2	$PdCl_2/Si_2O_{3.5}(CH_2)_3N{=}CH{-}C_5NH_4$		4.2	7.4	3.6
3	$PdCl_2/Si_2O_{3.5}(CH_2)_3NH{-}CH_2{-}C_5NH_4$		4.2	9.6	3.3
4	$PdCl_2/Si_2O_{3.5}(CH_2)_3N{=}C(CH_3){-}C_5NH_4$		5.8	11.3	3.2
5	$PdCl_2/Si_2O_{3.5}(CH_2)_3NH{-}CH(CH_3){-}C_5NH_4$		5.8	13.7	4.0

[a] Reaction conditions: $n(Pd^{2+}) : n(Cu_2O) : n(BQ) : n(Bu_4NBr) : n(PhOH) = 1:6:30:30:1000$, $T = 110\,^{\circ}C$, $t = 5$ h, THF as solvent.
[b] Pd in solution/total amount of Pd introduced.

Table 4. Recycle catalytic performance of $PdCl_2$/OIH **4b**[a]

Run	1	2	3	4	Mean value (%)
Y_{DPC} (%)	4.1	4.0	4.6	4.0	4.2
Pd loss[b] (wt%)	3.0	2.5	2.8	2.6	2.7

[a] Reaction conditions: $n(Pd^{2+}) : n(Cu_2O) : n(BQ) : n(Bu_4NBr) : n(PhOH) = 1:6:30:30:1000$, $T = 110\,^{\circ}C$, $t = 5$ h, THF as solvent and 3 Å MS not used, Pd loading = 5.8%.
[b] Pd in solution/total amount of Pd introduced.

Table 5. Catalytic performance comparison of $PdCl_2$–OIH **4b** and Pd–C[a]

Catalyst	Pd loading (wt%)	Y_{DPC} (%)	Pd loss[b] (wt%)
$PdCl_2$–OIH **4b**	5.8	13.7	4.0
Pd–C	5	3.2	20.9

[a] Reaction conditions: $n(Pd^{2+}) : n(Cu_2O) : n(BQ) : n(Bu_4NBr) : n(PhOH) = 1:6:30:30:1000$, $T = 110\,^{\circ}C$, $t = 5$ h, THF as solvent.
[b] Pd in solution/total amount of Pd introduced.

show that $PdCl_2$–OIH was more active and stable than the traditional supported catalyst Pd–C, probably due to the strong interaction between organic and inorganic moieties in the OIH. The organic moieties introduced into OIH not only enhance the catalytic activity, but also effectively resist Pd leaching.[29]

CONCLUSIONS

In this study, OIH was prepared using a sol–gel approach using APTES as silane coupling agent, and TEOS as precursor, then reacted with $PdCl_2(PhCN)_2$ to make heterogeneous catalysts $PdCl_2$–OIH. The reaction parameters such as temperature, pressure, solvent and inorganic cocatalyst affected the yield of DPC and Pd leaching significantly; Cu_2O and THF were chosen as the best partners for the supported heterogeneous catalyst $PdCl_2$–OIH. In the presence of Cu_2O and THF, the $PdCl_2$–OIH prepared from 2-actylpyridine revealed good catalytic activity and stability, since the yield of DPC reached 13.7% and Pd loss was 4.0% in solution. The yield of DPC remained almost unchanged; the mean yield was 4.2% and the mean Pd loss was 2.7% during four recycles. The $PdCl_2$–OIH was more active and stable compared with the traditional supported catalyst Pd–C under the same reaction conditions.

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