Alkoxycarbonylation and phenoxycarbonylation reactions catalyzed by a palladium(II) organometallic complex encaged in Y zeolite

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Abstract Catalytic routes for synthesis of alkyl benzoates by alkoxycarbonylation reactions and aryl benzoates by phenoxycarbonylation reactions of aryl iodides are described using a palladium–1,10-phenanthroline complex encaged in Y zeolite. Moderate to excellent yields (40–99 %) of various benzoates were obtained at low Pd loadings of 0.6 mol%. The catalyst could be effectively removed from the reaction mixture by a simple filtration process and was reused four times with only minor loss of activity. Furthermore, its catalytic activity was further highlighted by a comparison with another two supported Pd catalysts. The protocol has the advantages of easy handing, moderate to excellent yield, and catalyst recyclability.

Introduction

The functionalization of aryl halides is of major importance in the field of modern arene chemistry due to the ubiquity of aromatic and heteroaromatic units [1]. Aryl esters constitute integral parts of polymers, pharmaceuticals, and agrochemicals, as well as building blocks for organic synthesis and natural products. Typically, they are prepared via the reaction of acyl halides, anhydrides, or activated esters with O nucleophiles [2] or via esterification or transesterification reactions catalyzed by strong acids or bases which considerably limit the reaction scope [3]. For the preparation of functionalized benzoates, palladiumcatalyzed alkoxycarbonylations or phenoxycarbonylations of aryl halides in the presence of alcohols or phenols represent a valuable alternative (Scheme 1) [4, 5].

Palladium complexes have received considerable interest as powerful catalysts for alkoxycarbonylations and phenoxycarbonylations of aryl halides [6–11], but separation and recycling of the homogeneous catalysts still remains a big challenge. Hence, much effort has been made to immobilize them on diverse supports, such as activated carbon [12, 13], silica [14], MCM-41 [15], organic polymers [16], Fe₃O₄ [17], and ionic liquids [18] to create heterogeneous catalysts. In terms of both academia and industry, developing more active heterogeneous catalytic systems is imperative and merits further study.

In continuation of our studies into the heterogenization of homogeneous catalysts, we have utilized well-defined supercages of Y zeolite to encapsulate the $[PdCl_2(phen)]$ (phen = 1,10-phenanthroline) molecules, i.e., PdCl₂ (phen)@Y (Scheme 1), and the immobilized catalyst has been successfully used by our team to carry out the oxidation carbonylation of glycerol [19]. In order to extend the application of the active Pd heterogeneous catalyst, in this paper, we wish to explore the alkoxycarbonylation and phenoxycarbonylation reactions of aryl iodides for synthesis of benzoates catalyzed by PdCl₂(phen)@Y. Furthermore, its catalytic recyclability was further highlighted by a comparison with those of two other catalysts prepared by impregnation on the zeolite or graft polymer method under the same reaction conditions.

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Scheme 1 Palladium-catalyzed alkoxycarbonylations and phenoxycarbonylations of aryl halides



Experimental

Materials

NaY zeolite was purchased from Nanjing Nanda Surface and Interface Chemical Engineering and Technological Research Center Co. Ltd., China. The chloromethylated polystyrene (PS-Cl) was supplied by Tianjin Nankai Hecheng Technology Co. Ltd., China. Palladium nitrate dihydrate, palladium chloride, potassium carbonate, 1,10phenanthroline monohydrate (phen·H₂O), 5-nitro-1,10phenanthroline, aryl halides, triethylamine, alcohols, phenols, pyridine, naphthalene, and methyl benzoate were of analytical reagent grade and commercially available. NaY molecular sieves were calcined at 350 °C for 3 h before use.

Preparation of catalysts

[PdCl₂(phen)] was prepared according to the literature [20]. The PdCl₂(phen)@Y catalyst was prepared by a stepwise method according to our recent publication [19], and the structure and composition of the solid catalyst were characterized by FTIR, UV–Vis, N₂ sorption, BET, TG/ DTA, XRD, and XPS techniques. For comparison, the [PdCl₂(phen)] complex was absorbed outside Y zeolite by impregnation, PdCl₂(phen)/Y, or immobilized on PS-Cl by graft method [21], PdCl₂(phen-PS), respectively (see the detailed data for preparation and characterization of the catalysts in Online Resource).

General procedure for the alkoxycarbonylation reaction

The catalytic reactions were carried out in a 150-ml stainless steel autoclave equipped with a mechanical stirrer. Palladium catalyst (0.06 mmol), aryl iodide (2.04 g, 10 mmol), Et_3N (3.04 g, 30 mmol), and alcohol (20 ml) were loaded into the reactor. The autoclave was purged three times with CO and pressurized to 0.5 MPa. The reaction was carried out at 100 °C for the appropriate time. After the reaction, the reactor was cooled to room temperature and depressurized. The reaction mixture was centrifuged at 5,000 rpm for 10 min, and the clear supernatant to which was added naphthalene as an internal standard was analyzed with GC. For the study of substrate scope, after completion of the reaction, the reaction mixture was centrifuged at 5,000 rpm for 10 min and the clear supernatant was diluted with saturated NH₄Cl and extracted with diethyl ether. The organic layer was dried over anhydrous Na₂SO₄, and evaporated under vacuum after filtration. The residue obtained was purified by column chromatography (silica gel, 200–300 mesh; petroleum ester–ethyl acetate, 50:1) to afford the pure products. All products were confirmed by ¹H and ¹³C NMR analyses. For the recycling experiments, the heterogeneous catalyst was separated by centrifugation from the reaction mixture, washed three times with the reaction solvent (methanol), and then engaged in a new catalytic cycle under the same reaction conditions.

General procedure for the phenoxycarbonylation reaction

The catalytic reactions were carried out in a 150-ml stainless steel autoclave equipped with a mechanical stirrer. Palladium catalyst (0.06 mmol), PhI (2.04 g, 10 mmol), Et₃N (3.04 g, 30 mmol), phenol (1.13 g, 12 mmol), and solvent N,N-dimethylacetamide (DMAc, 20 ml) were loaded into the reactor. The autoclave was purged three times with CO and pressurized to 2 MPa. The reaction was carried out at 100 °C for 4 h. After the reaction, the reactor was cooled to room temperature and depressurized. The reaction mixture was centrifuged at 5,000 rpm for 10 min, and the clear supernatant to which was added naphthalene as an internal standard was analyzed with GC. The clear supernatant was diluted with saturated NH₄Cl and extracted with diethyl ether. The organic layer was dried over anhydrous Na₂SO₄ and evaporated under vacuum after filtration. The residue obtained was purified by column chromatography (silica gel, 200-300 mesh; petroleum ester-ethyl acetate, 50:1) to afford the pure products. All products were confirmed by ¹H and ¹³C NMR analyses. For the recycling experiments, the heterogeneous catalyst was separated by centrifugation from the reaction mixture, washed three times with the reaction solvent (DMAc), and then engaged in a new catalytic cycle under the same reaction conditions.

Spectral data of the products

NMR spectra were recorded on 400 MHz Bruker AV400 spectrometers. Chemical shifts for protons are reported in

parts per million (ppm) downfield from TMS with the solvent resonance (CDCl₃: 7.26) as the internal standard. Chemical shifts for carbon are given in ppm and referenced to the carbon resonances of the solvent (CDCl₃: 77.16). Coupling constants (J) are reported in Hz and refer to apparent peak multiplicities.

Methyl 4-Anisate (**1a**): white solid; ¹H NMR (400 MHz, CDCl₃): δ 7.986 (d, J = 8.8 Hz, 2H), 6.907 (d, J = 8.8 Hz, 2H), 3.867 (s, 3H), 3.846 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.9, 163.4, 131.7, 122.7, 113.7, 55.5, 51.9.

Methyl 4-methylbenzoate (**1b**): colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 7.922 (d, J = 8.2 Hz, 2H), 7.215 (d, J = 8.2 Hz, 2H), 3.883 (s, 3H), 2.386 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 167.2, 143.6, 129.7, 129.1, 127.5, 51.9, 21.7.

Methyl 3-methylbenzoate (**1c**): colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 7.808–7.838 (m, 2H), 7.279–7.329 (m, 2H), 3.872 (s, 3H), 2.358 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 167.2, 138.1, 133.6, 130.1, 128.2, 126.7, 52.0, 21.2.

Methyl 4-chlorobenzoate (1d): colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 7.962 (d, J = 8.4 Hz, 2H), 7.400 (d, J = 8.4 Hz, 2H), 3.905 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.1, 139.3, 131.0, 128.7, 52.2.

Methyl 3-chlorobenzoate (**1e**): colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 8.009 (t, J = 1.6 Hz, 1H), 7.913 (dt, $J_3 = 8.0$ Hz, $J_4 = 1.2$ Hz, 1H), 7.504–7.532 (m, 1H), 7.371 (t, J = 8.0 Hz, 1H), 3.918 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 165.9, 134.6, 133.0, 132.0, 129.7, 127.7, 52.4.

Methyl 4-fluorobenzoate (**1f**): colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 8.005–8.044 (m, 2H), 7.052–7.098 (m, 2H), 3.883 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 167.1, 166.2, 164.6, 132.2, 132.1, 126.5, 115.7, 115.4, 52.2.

Ethyl benzoate (**1g**): colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 8.036–8.057 (m, 2H), 7.536 (t, J = 7.2 Hz, 1H), 7.422 (t, J = 8.0 Hz, 2H), 4.376 (q, J = 7.2 Hz, 2H), 1.389 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.7, 132.8, 130.6, 129.6, 129.4, 128.4, 61.0, 14.4.

Propyl benzoate (**1h**): colorless oil; 1H NMR (400 MHz, CDCl₃): δ 8.042 (d, J = 7.6 Hz, 2H), 7.532 (t, J = 7.6 Hz, 1H), 7.421 (t, J = 7.6 Hz, 2H), 4.280 (t, J = 6.8 Hz, 2H), 1.788 (sext, J = 7.2 Hz, 2H), 1.028 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.7, 132.8, 130.6, 129.6, 128.4, 66.6, 22.2, 10.6.

n-Butyl benzoate (**1i**): colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 8.036–8.059 (m, 2H), 7.519–7.562 (m, 1H), 7.409–7.447 (m, 2H), 4.329 (t, J = 6.4 Hz, 2H), 1.756 (quint, J = 6.8 Hz, 2H), 1.484 (sext, J = 8.0 Hz, 2H), 0.984 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz,

CDCl₃): δ 166.8, 132.9, 130.7, 129.6, 128.4, 64.9, 30.9, 19.4, 13.8.

Benzyl benzoate (**1j**): colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 8.108–8.136 (m, 2H), 7.577 (t, J = 7.2 Hz, 1H), 7.370–7.496 (m, 7H), 5.404 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 166.5, 136.2, 133.1, 130.2, 129.8, 128.7, 128.4, 128.3, 128.2, 66.7.

Isopropyl benzoate (**1k**): colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 8.042 (d, J = 8.0 Hz, 2H), 7.534 (t, J = 7.6 Hz, 1H), 7.423 (t, J = 8.0 Hz, 2H), 5.260 (quint, J = 6.4 Hz, 1H), 1.372 (d, J = 6.4 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 166.2, 132.8, 131.1, 129.6, 128.4, 68.4, 22.1.

Cyclohexyl benzoate (11): colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 8.045–8.069 (m, 2H), 7.507–7.550 (m, 1H), 7.403–7.441 (m, 2H), 5.006–5.069 (m, 1H), 1.263–1.967 (m, 10H); ¹³C NMR (100 MHz, CDCl₃): δ 166.0, 132.7, 131.1, 129.6, 128.3, 73.0, 31.7, 25.5, 23.7.

Phenyl benzoate (**2a**): white solid; ¹H NMR (400 MHz, CDCl₃): δ 8.266 (d, J = 8.0 Hz, 2H), 7.681 (t, J = 7.6 Hz, 1H), 7.558 (t, J = 7.6 Hz, 2H), 7.482 (t, J = 7.6 Hz, 2H), 7.264–7.342 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 165.3, 151.1, 133.7, 130.3, 129.7, 129.6, 128.7, 126.0, 121.8.

4-Methoxyphenyl benzoate (**2b**): white solid; ¹H NMR (400 MHz, CDCl₃): δ 8.207 (d, J = 8.0 Hz, 2H), 7.636 (t, J = 8.0 Hz, 1H), 7.512 (t, J = 8.0 Hz, 2H), 7.143 (d, J = 9.2 Hz, 2H), 6.950 (d, J = 9.2 Hz, 2H), 3.830 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 165.7, 157.5, 144.6, 133.6, 130.3, 129.8, 128.7, 122.6, 114.7, 55.8.

4-Tolyl benzoate (**2c**): white solid; ¹H NMR (400 MHz, CDCl₃): δ 8.244 (d, J = 7.6 Hz, 2H), 7.665 (t, J = 7.6 Hz, 1H), 7.542 (t, J = 8.0 Hz, 2H), 7.261 (d, J = 8.0 Hz, 2H), 7.135 (d, J = 8.0 Hz, 2H), 2.413 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 165.5, 148.9, 135.6, 133.6, 130.3, 130.1, 129.8, 128.7, 121.5, 21.0.

3-Tolyl benzoate (**2d**): colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 8.257–8.280 (m, 2H), 7.643–7.687 (m, 1H), 7.544 (t, J = 8.0 Hz, 2H), 7.363 (t, J = 8.0 Hz, 1H), 7.078–7.146 (m, 3H), 2.440 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 165.3, 151.0, 139.7, 133.5, 130.2, 129.7, 129.2, 128.6, 126.7, 122.3, 118.7, 21.3.

2-Tolyl benzoate (2e): colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 8.350 (d, J = 8.0 Hz, 2H), 7.717 (t, J = 7.6 Hz, 1H), 7.600 (t, J = 7.6 Hz, 2H), 7.341–7.388 (m, 2H), 7.251–7.304 (m, 2H), 2.353 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 164.8, 149.6, 133.6, 131.2, 130.3, 130.1, 129.5, 128.6, 127.0, 126.1, 122.0, 16.2.

4-*Tert*-butylphenyl benzoate (**2f**): white solid; ¹H NMR (400 MHz, CDCl₃): δ : 8.212 (d, J = 8.0 Hz, 2H), 7.637 (t, J = 7.6 Hz, 1H), 7.434–7.534 (m, 4H), 7.145 (d, J = 8.8 Hz, 2H), 1.349 (s, 9H); ¹³C NMR (100 MHz,

Table 1 Palladium-catalyzed alkoxycarbonylation of iodobenzene with methanol

+ CH ₃ OH + CO $\xrightarrow{Pd cat.}$									
Entry	Catalyst	Base	<i>T</i> (°C)	P _{CO} (MPa)	<i>t</i> (h)	Yield ^a (%)			
1	PdCl ₂ (phen)	Et ₃ N	100	0.5	1	99			
2	PdCl ₂ (phen)	Pyridine	100	0.5	1	21			
3	PdCl ₂ (phen)	K ₂ CO ₃	100	0.5	1	99			
4 ^b	PdCl ₂ (phen)	Et ₃ N	80	0.5	1.5	99			
5	PdCl ₂ (phen)	Et ₃ N	100	0.3	1.5	99			
6	PdCl ₂ (phen)	Et ₃ N	100	0.1	1.5	86			
7 ^c	PdCl ₂ (phen)	Et ₃ N	100	0.5	1	99			
8 ^d	PdCl ₂ (phen)	Et ₃ N	100	0.5	1.5	97			
9 ^e	PdCl ₂ (phen)@Y	Et ₃ N	100	0.5	1	99			

Reaction conditions: Pd (0.7 mol%), PhI (10 mmol), Et₃N (30 mmol), methanol (20 ml)

^a GC yield

^b 86 % conversion and 85 % yield obtained at 80 °C after 1 h

^c Pd (0.5 mol%)

^d Pd (0.2 mol%)

^e Pd (0.6 mol%)

CDCl₃): δ 165.5, 148.8, 148.7, 133.6, 130.3, 129.9, 128.7, 126.5, 121.1, 34.7, 31.6.

4-Chlorophenyl benzoate (**2g**): white solid; ¹H NMR (400 MHz, CDCl₃): δ 8.187–8.211 (m, 2H), 7.632–7.676 (m, 1H), 7.504–7.542 (m, 2H), 7.381–7.411 (m, 2H), 7.158–7.196 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 165.1, 149.6, 133.9, 131.4, 130.3, 129.7, 129.3, 128.8, 123.2.

2,3-Dichlorophenyl benzoate (**2h**): white solid; ¹H NMR (400 MHz, CDCl₃): δ 8.267 (d, J = 7.2 Hz, 2H), 7.702 (t, J = 7.2 Hz, 1H), 7.567 (t, J = 7.6 Hz, 2H), 7.438 (dd, $J_1 = 7.6$ Hz, $J_2 = 1.2$ Hz, 1H), 7.304 (t, J = 8.0 Hz, 1H), 7.249 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.6$ Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 163.1, 143.4, 134.4, 132.2, 130.7, 130.0, 128.9, 128.8, 128.2, 128.1, 125.1, 121.8.

2,4,6-Trichlorophenyl benzoate (**2i**): white solid; ¹H NMR (400 MHz, CDCl₃): δ 8.248 (d, J = 7.6 Hz, 2H), 7.689 (t, J = 7.6 Hz, 1H), 7.549 (t, J = 7.6 Hz, 2H), 7.428 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 163.1, 147.1, 143.4, 134.4, 132.2, 130.7, 130.0, 128.9, 128.8, 128.2, 128.1, 125.5, 121.8.

Results and discussion

Catalytic activity

With respect to the development of an efficient heterogeneous protocol for alkoxycarbonylation, the reaction of iodobenzene with methanol was chosen as a model reaction in the first stage of our study, and the influences of various reaction parameters such as base, temperature, CO pressure, and Pd dosage were studied (Table 1).

Using iodobenzene and methanol as substrates, [PdCl₂(phen)] with a low dosage of palladium catalyst (0.7 mol%) at 100 °C and 0.5 MPa CO afforded remarkably high activity with a complete conversion and 99 % yield (Table 1, entry 1). The choice of base was essential for the reaction. Pyridine was inefficient for this transformation (Table 1, entry 2). Although K₂CO₃ (Table 1, entry 3) and Et₃N both performed well, on considering the economy of organic amines over potassium salts, Et₃N was chosen as the base for further optimization. We observed good conversion of iodobenzene (86 %) and yield of methyl benzoate (85 %) when the reaction was carried out at 80 °C after 1 h. If the reaction time was prolonged to 1.5 h at 80 °C, a complete conversion and 99 % yield were also achieved (Table 1, entry 4). Increasing the CO pressure from 0.1-0.5 MPa did increase the yield of the desired product, and to our delight, under optimized conditions, the pressure could be reduced to 0.1 MPa of CO, and an 86 % yield of product was still obtained (Table 1, entries 1, 5, and 6). Encouraged by the high reactivity of this palladium-catalyzed system, we tried to employ a low catalyst loading. When the reaction was carried out with 0.5 mol% [PdCl₂(phen)], 100 % conversion of iodobenzene was achieved after 1 h, which was accompanied by 99 % yield for the product (Table 2, entry 7). Moreover, with a catalyst loading as low as 0.2 mol%, the high activity of the [PdCl₂(phen)] system was retained with 97 % yield after a

Table 2 Alkoxycarbonylations of various aryl iodides and alcohols

2	$R^{1} \underbrace{\prod_{l}}_{ll} + R^{2}OH + CO \xrightarrow{PdCl_{2}(phen)@Y}{NEt_{3}, 100 °C, 0.5 MPa} R^{1} \underbrace{\prod_{l}}_{ll} O R^{2}$					
Entry	R ¹	R^2	1a-m Product	Yield ^a (%)		
1	p-OMe	Me		98		
2	<i>p</i> -Me	Me		98		
3	o-Me	Me		97		
4	p-Cl	Me		98		
5	<i>m</i> -Cl	Me		98		
6	p-F	Me		98		
7	Н	Et		98		
8	Н	ⁿ Pr		90		
9	Н	ⁿ Bu	th O O	97		
10 ^b	Н	PhCH ₂		94		
11 [°]	Н	ⁱ Pr		40		
12 ^c	Н	Су		40		



Reaction conditions: PdCl₂(phen)@Y (0.6 mol%), aryl iodide (10 mmol), Et₃N (30 mmol), alcohol (20 ml), 0.5 MPa, 1 h, 100 °C ^a Isolated yield

^b 2 h

- 2 r

° 3 h

prolonged reaction time to 1.5 h (Table 1, entry 8). With the optimized reaction conditions in hand, the activity of the heterogeneous catalyst $PdCl_2(phen)@Y$ was investigated. Fortunately, a 100 % conversion of iodobenzene and 99 % of yield were obtained (Table 1, entry 9). The similar high activity of encapsulated complexes is because of site isolation of the complexes in zeolitic microcapsular reactors via the quasi-homogeneous catalysis [22, 23].

Substrate scope

Next, we investigated the activity of $PdCl_2(phen)@Y$ for various substrates in alkoxycarbonylation reactions, and the results are summarized in Table 2.

As shown in Table 2, a range of aryl iodides bearing either an electron-withdrawing group or an electrondonating group were highly effectively carbonylated in methanol, providing the desired ester products. They showed excellent functional group tolerance and gave clean conversion to the benzoate products without competing formation of other byproducts. Iodobenzene with methoxyl, methyl, chlorine, and fluorine groups all afforded high yields of the benzoate (97–98 %) (Table 2, entries 1–6).

Next, the alkoxycarbonylations of iodobenzene with various alcohols were investigated (Table 2, entries 7-13). The results of alkoxycarbonylation of iodobenzene with various alcohols demonstrated that the chemical properties of groups bearing on the substrates from primary alcohol to tertiary alcohol had significant effects on the yields. Iodobenzene reacted efficiently with primary alcohols, such as ethanol, n-propanol, n-butanol, and benzyl alcohol to give the corresponding benzoates in excellent yields (94-98 %), although for benzyl alcohol a prolonged reaction time was required (Table 2, entries 7-10). However, with secondary alcohols (isopropanol and cyclohexanol), a lower yield (40 %, respectively) of carbonylation product was obtained after 3 h (Table 2, entries 11 and 12). Unfortunately, when t-butanol was used as a nucleophile, no desired product could be detected, presumably due to the high steric bulk of the incoming alcohol impeding its coordination with the metal center [24] (Table 2, entry 13).

Encouraged by the successful application of $PdCl_2(-phen)@Y$ in the alkoxycarbonylations of aryl iodides with alcohols, we expected to generalize the application of this catalyst in the phenoxycarbonylation reactions. Considering the lower nucleophilicity of phenols than the alcohols, all phenoxycarbonylation reactions were conducted under 100 °C and 2 MPa for 4 h. As shown in Table 3, similarly to alcohols, $PdCl_2(phen)@Y$ as the catalytic system for the phenoxycarbonylation reactions of iodobenzene with various phenols proved to be exceptionally active. To our delight, either electron-withdrawing or electron-donating substituents on the nucleophiles worked quite well in this system, giving the desired products in excellent yields (93–97 %).

Catalyst recycling

One of the main utilities of heterogenization is to enhance the life of the resulting catalyst. To investigate the reusability of $PdCl_2(phen)@Y$, recycling experiments were carried out for alkoxycarbonylation and phenoxycarbonylation reactions of iodobenzene. After each experiment, the catalyst was separated by simple filtration, washed, and then subjected to the next run under the same experimental conditions. The catalytic run was repeated with further addition of substrates in appropriate amounts, and the yields of the final products were comparable to that of the original run. The results presented in Table 4 showed that the $PdCl_2(phen)@Y$ catalyst exhibited good reusability through five recycles in carbonylation reactions of iodobenzene (Table 4, entries 1 and 2).

In order to confirm the impact of the supercage-like structure of Y zeolite on the recyclability, the [PdCl₂(phen)] complex was immobilized on Y zeolite by impregnation method resulting in PdCl₂(phen)/Y, or immobilized on PS-Cl by graft polymer method resulting in the polymer-bound catalyst PdCl₂(phen-PS), respectively. For the preparation of PdCl₂(phen)/Y, we soaked Y zeolite in a concentrated



 Table 3 Phenoxycarbonylations of iodobenzene with various phenols

Reaction conditions: $PdCl_2(phen)@Y$ (0.6 mol%), PhI (10 mmol), Et_3N (30 mmol), phenol (12 mmol), DMAc (20 ml), 2 MPa, 4 h, 100 °C

^a Isolated yield

solution of $[PdCl_2(phen)]$ in DMSO solution for 24 h. As the diameter of $[PdCl_2(phen)]$ (~9.0 Å) [19] is too large to effectively penetrate through the zeolite cage's free aperture (~7.4 Å) [25], the molecules were adsorbed onto the exterior surface of Y zeolite rather than entering the zeolite cages. A light yellow solid was obtained upon washing, which exhibited the same color as the neat complex, but a different color with PdCl₂(phen)@Y (pink solid). The polymer-bound

 Table 4
 Recycling efficiency of heterogeneous Pd catalysts for carbonylation reactions of iodobenzene

Entry	Catalyst	Yield of the product at recycles (%)					
		Fresh	1st	2nd	3rd	4th	
1 ^a	PdCl ₂ (phen)@Y	99	95	91	86	85	
2 ^b	PdCl ₂ (phen)@Y	96	93	90	87	82	
3 ^a	PdCl ₂ (phen)/Y	97	83	65	36	28	
4 ^a	PdCl ₂ (phen-PS)	95	84	72	65	49	

 a Reaction conditions for alkoxycarbonylation reaction: Pd (0.6 mol%), PhI (10 mmol), Et_3N (30 mmol), methanol (20 ml), 0.5 MPa, 100 °C, 1 h

 $^{\rm b}$ Reaction conditions for phenoxycarbonylation reaction: Pd (0.6 mol%), PhI (10 mmol), Et_3N (30 mmol), phenol (12 mmol), DMAc (20 ml), 2 MPa, 100 $^{\circ}\text{C}$, 4 h

catalyst PdCl₂(phen-PS) was prepared by coordination of PdCl₂ with 5-NH₂-phen grafted on PS-Cl. Comparative tests for the recyclability were conducted, and the results are presented in Table 4. Under the same reaction conditions as PdCl₂(phen)@Y for alkoxycarbonylation of iodobenzene with methanol, the PdCl₂(phen)/Y gave 97, 83, 65, 36, and 28 % yields of methyl benzoate for successive reaction cycles, and the polymer-bound catalyst PdCl₂(phen-PS) gave 95, 84, 72, 65, and 49 % yields (Table 4, entries 3 and 4). Hence, the yields for both of these catalysts dramatically decreased upon recycling. Obviously, the recyclability of PdCl₂(phen)@Y was much better than that of the catalysts prepared by impregnation or graft method under the same conditions. The good recyclability may be attributed to the spatial restriction of the isolated nanocages and the smaller pore entrances of Y zeolite, as well as the strong chelation affinity of phen ligand toward palladium preventing the catalyst inactivation.

Proposed catalytic mechanism

Carbonylations of aryl halides on the PdCl₂(phen)@Y catalyst may follow a similar mechanism [26] but within the supercages of Y zeolite via a quasi-homogeneous process, as illustrated in Scheme 2. The catalytic cycle starts with the formation of the coordinatively unsaturated $[Pd^{0}L]Y I (L = phen)$ by reducing $[PdCl_{2}(phen)]Y$ with CO. Next, oxidative addition of aryl iodide to a Pd⁰ species takes place to form the aryl Pd^{II} complex II. After coordination and insertion of CO, the respective acyl Pd^{II} complexes III are produced. Subsequent nucleophilic attack of alcohols or phenols gives the benzoate as the last product. Finally, in the deprotonation by the base Et₃N, the reductive elimination of $[HPd^{II}IL]Y IV$ might take place giving Et₃N·HI and the active Pd⁰ species [LPd⁰]Y I, which starts the next reaction cycle [8, 27].



Scheme 2 Proposed mechanism of the palladium-catalyzed alkoxycarbonylation and phenoxycarbonylation reactions of aryl iodides

Conclusion

In summary, we have successfully applied the Y zeolite encapsulated PdCl₂(phen) complex in the alkoxycarbonylation and phenoxycarbonylation reactions of aryl iodides. The catalyst exhibits high activity, affording a diverse range of benzoate products in good to excellent yields under mild conditions. The catalyst is stable to the reaction conditions and can be recycled four times. Furthermore, its recyclability was further highlighted by a comparison with that of the [PdCl₂(phen)] complex absorbed on Y zeolite or bound on PS-Cl. The easy separation and availability make such supported palladium catalyst an interesting alternative to the homogeneous catalysts in carbonylations.

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