Palladium-1,10-phenanthroline complex encaged in Y zeolite: An efficient and highly recyclable heterogeneous catalyst for aminocarbonylation

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ABSTRACT

A promising route for catalytic synthesis of amides by aminocarbonylation of aryl iodides with amines is described using a palladium-1,10-phenanthroline complex encaged in Y zeolite. Complete conversions for aryl iodides and good to excellent yields (71–97%) of various amides were obtained at low Pd loadings of 0.6 mol%. The turnover frequency (TOF) could be up to 139 h^{-1}. A satisfactory yield was obtained even after the catalyst was reused 16 times and the total turnover number (TON) for the 16 cycles was up to 2250. As evidenced by atomic absorption spectrophotometry, UV–vis spectroscopy and X-ray photoelectron spectroscopy, the palladium complex could well nestle down in the supercages of the zeolite without leaching during the recycling process. The significantly enhanced recyclability could be attributed to the double-protection strategy provided by the ligand and the zeolite structure for Pd^0 species generated in situ within supercages preventing the migration and leaching of palladium. The supported catalyst has the advantages of easy handing, good to excellent yields, and outstanding recycling capacity for aminocarbonylation reactions of aryl iodides.
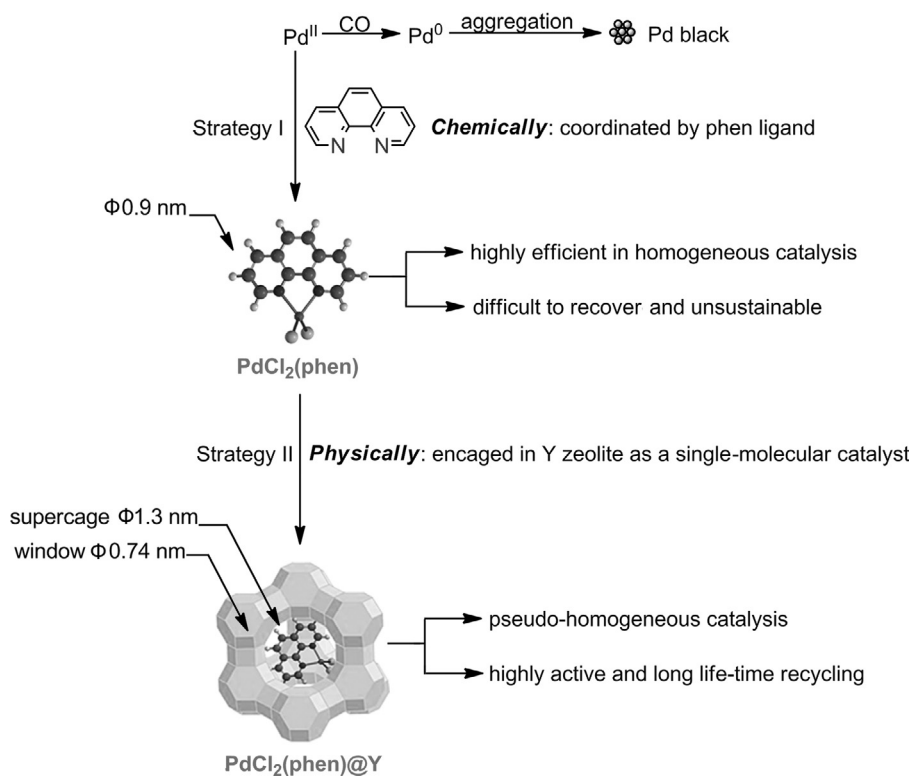
1. Introduction

Amides represent an important class of compounds and are ubiquitous in the pharmaceutical industry, materials science, and chemical biology [1–5]. Palladium-catalyzed aminocarbonylation is an alternative technique for amide synthesis that has a number of advantages over traditional synthesis methods that use carboxylic acid derivatives and amines. This new technique has emerged in recent years as the most promising direct route for the atom-economical and cost effective synthesis of amides, producing the amides from inexpensive and easily available feedstocks such as carbon monoxide and organic halides in the presence of suitable amines [6–11]. Much of the recent research effort has focused on the development of various Pd complexes as catalytic systems for the aminocarbonylation of aryl halides [12]. In order to address the problem of separation and reusability of expensive Pd homogeneous catalysts, researchers have immobilized palladium complexes on various supports such as activated carbon [13,14], silica [15,16], MCM-41 [17], organic polymer [18–20], ionic liquid [21,22], MOF [23] and ZIF-8 [24] to create heterogeneous catalysts. However, all these heterogeneous catalytic systems reported have limited recycling capacity no more than a few times, which is not quite enough in terms of practical application.

The general difficulty in using currently known heterogeneous Pd catalysts arises from the unique reaction mechanism involving a Pd^0 state. Numerous reported works have shown that the catalytic active state in aminocarbonylation reactions is a Pd^0 species [25,26]. In cases where Pd^{II} is used, in situ reduction to Pd^0 is known to occur during the reaction, and this reduced Pd^0 species most likely leaches into the reaction media [27,28]. Furthermore, the reversible dissolution and re-deposition of Pd^0 can result in the agglomeration of Pd^0 species into large Pd nanoparticles (Pd black), which can cause a loss of metal dispersion and surface area of the catalyst [29]. Thus, in the terms of both academia and industry, developing new strategies to protect Pd^0 in order to achieve high activity and reusability are imperative and merit further study.

Herein, we report a facile protocol for the synthesis of amides by aminocarbonylation of aryl iodides using an efficient and highly recyclable heterogeneous catalyst PdCl$_2$(phen)@Y (phen = 1,10-phenanthroline) utilizing a double-protection strategy against Pd degradation (Scheme 1). Note that the [PdCl$_2$(phen)] and the corresponding Y zeolite immobilized catalyst have been successfully used by our team to carry out the oxidation carbonylation of glycerol [30]. In order to extend the application of the active Pd heterogeneous catalyst, we employed the catalyst in aminocarbonylation of aryl iodides and found that this catalyst afforded

Scheme 1. Physically and chemically double-protection strategy: combining the ligand coordination with the Y zeolite encapsulation for PdCl$_2$(phen)@Y catalyst.

complete conversions of various aryl iodides at low Pd loading. More importantly, the catalyst was stable, showed negligible metal leaching, and retained high activity for at least 16 successive runs without any additional activation treatment. Furthermore, we also discussed the underlying reason of the enhanced recyclability.

2. Experimental

2.1. Materials

NaY zeolite was purchased from Nanjing Nanda Surface and Interface Chemical Engineering and Technological Research Center Co. Ltd. (China). 1,10-phenanthroline monohydrate (phen·H$_2$O) was purchased from Alfa Aeser. Palladium nitrate dihydrate, palladium chloride, potassium carbonate, aryl iodides, amines, pyridine, naphthalene and N,N-diethylbenzamide were of analytical reagent grade and commercially available. 5% Pd/C was purchased from Shanxi Rock New Materials Co. Ltd. (China). All solvents were distilled prior to use. NaY zeolites were calcined at 350 °C for 3 h before used.

2.2. Preparation of catalysts

The preparation procedures of complexes encapsulated in Y zeolite can be found in our recent publication [30]. Pd metal in Y zeolite was prepared according to the literature [31]. [PdCl$_2$(phen)] absorbed on Y zeolite was prepared as follows. [PdCl$_2$(phen)] (30 mg, 0.08 mmol) was completely dissolved in DMSO (5 ml) at 80 °C. Then, NaY (0.4 g) was added and stirred overnight. After filtering, the obtained yellow solid was washed by the reaction solvent DMAc (5 ml) and then engaged in the aminocarbonylation reaction. The loaded Pd content was indirectly calculated according to AAS analysis of the residual Pd in the filtrate.

2.3. The procedure for the aminocarbonylation reaction

The catalytic reactions were carried out in a 150 ml stainless steel autoclave equipped with a mechanical stirrer. Palladium catalyst (0.07 mmol), aryl iodide (10 mmol), amine (20 mmol), base (30 mmol) and solvent (15 ml) were loaded into the reactor. The autoclave was purged three times with CO and pressurized to 1.5 MPa with CO at room temperature. The reaction was carried out at 130 °C for appropriate time. After the reaction, the reactor was cooled to room temperature and depressurized. The reaction mixture was centrifuged at 5000 rpm for 10 min and the clear supernatant which was added naphthalene as an internal standard was analyzed with GC. For the study of substrate scope, after completion of the reaction, the catalyst was centrifuged at 5000 rpm for 10 min and the clear supernatant was diluted with 20% HCl and extracted with diethyl ether. The organic layer was washed with saturated NaHCO$_3$ and NaCl solutions, respectively, dried over anhydrous Na$_2$SO$_4$, and evaporated under vacuum after filtration. The residue obtained was purified by column chromatography (silica gel, 200–300 mesh; petroleum-ethyl acetate, 20:1) to afford the pure products. All products were confirmed by ^{1}H and ^{13}C NMR analyses. For the recycling experiments, the solid 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.

2.4. Physico-chemical measurements

The UV–vis analyses were performed on a Shimadzu UV-2550 spectrophotometer with the integration sphere diffuse reflectance attachment. The FTIR spectra in KBr pellet were recorded on a Bruker Equinox 55 FTIR spectrophotometer in the range 400–4000 cm^{-1}. N$_2$ adsorption–desorption experiment was conducted at -196 °C with a Quantachrome Autosorb-1-C/TCD/MS.

Prior to the experiment, the sample was degassed at 200 °C for 6 h. The surface area was obtained from the adsorption branch by means of the BET model in a relative pressure ranging from 0.05 to 0.30; the pore volumes were calculated using the BJH model. The total pore volumes were calculated from the amount of N_2 vapour adsorbed at a relative pressure of 0.99. Thermogravimetric analysis of the encapsulated samples was conducted on PerkinElmer TGA-7 instrument at a heating rate of 10 °C under an air atmosphere. The palladium contents of catalysts were measured by AAS using a PerkinElmer AA-300 spectrophotometer. The XRD data were collected with a Philip X-Pert Pro X-ray diffraction instrument in the 2θ range 5–55°. XPS was performed in a VG multilab 2000 spectrometer, using an Mg–Al Kα X-ray source with the passing energy flow of 100 eV. The samples were degassed in a chamber at 5×10^{-10} mbar at room temperature. The C_{1s} transition was adjusted to 284.8 eV. NMR spectra were recorded on 400 MHz Bruker AV400 spectrometers. Chemical shifts for protons are reported in parts per million (ppm) down field from TMS with the solvent resonance ($CDCl_3$: 7.26) as the internal standard. Chemical shifts for carbon were given in ppm that also referenced to the carbon resonances of the solvent ($CDCl_3$: 77.16). GC–MS analyses were performed in an Agilent 6890/5973 GC–MS apparatus equipped with a split/splitless injection system and FID. The capillary column was an Agilent HP-5MS (30 m × 0.25 mm × 0.25 μm). Helium (1.0 ml min^{-1}) was used as the carrier gas. GC analysis was conducted on Agilent GC 1790 equipped with a HP-5 capillary column and a flame ionization detector.

3. Results and discussion

3.1. Synthesis and characterization of the heterogeneous catalysts

We utilize well-defined supercages of commercial Y zeolite to encapsulate [PdCl$_2$(phen)] molecule as a single-molecular catalyst (Scheme 1). The free aperture of the supercage (~7.4 Å) of Y zeolite is too small for any migration of [PdCl$_2$(phen)] (~9.0 Å) [30] to neighboring cages or to the liquid phases. On the other hand, the cage itself is large enough to provide the catalyst with the required catalytic environment (internal diameter ~13 Å) [32]. Thus, a catalyst molecule can nest within the cage, where it functions like a pseudo-homogeneous catalyst while remaining separated from the bulk population of catalysts. Moreover, we had attempted to encapsulate the [PdCl$_2$Bipy] and [PdCl$_2$(2,9-Me$_2$phen)] complexes in supercages of Y zeolite by the same procedures respectively but failed to do so. This failure could be explained by the fact that the diameter of [PdCl$_2$(Bipy)] (~6.7 Å) is too small to be stably encapsulated in supercages of Y zeolite and the diameter of the ligand 2,9-Me$_2$phen (~7.7 Å) is too large to effectively penetrate through the zeolite-cage free-aperture (~7.4 Å) [33]. The same characteristic adsorptions of the neat complex with the encapsulated catalysts did not observed in FTIR spectra.

The formation and encapsulation of the [PdCl$_2$(phen)] complex in Y zeolite were confirmed by UV–vis spectra, as shown in Fig. 1. The figure makes it evident that after complexation and sufficient Soxhlet extraction, there is an obvious band at 277 nm present in the spectra of the PdCl$_2$(phen)@Y sample corresponding to the characteristic absorption peak of [PdCl$_2$(phen)] [34]. This same peak does not occur for the Y sample, strongly indicating the formation of a [PdCl$_2$(phen)] complex in the catalyst.

In order to obtain an insight into the oxidation state and coordination environment of palladium in the PdCl$_2$(phen)@Y catalyst, X-ray photoelectron spectroscopy (XPS) experiments were performed. Carbon, nitrogen, palladium, and chlorine all appeared in an XPS elemental survey scan of PdCl$_2$(phen)@Y (Fig. 2a). The Pd 3d$_{3/2}$ and Pd 3d$_{5/2}$ binding energies of PdCl$_2$(phen)@Y were
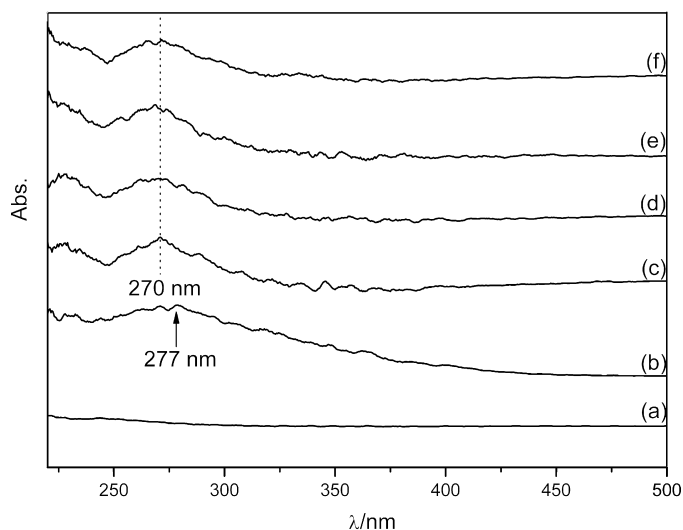

Fig. 1. UV–vis spectra of samples: (a) Y zeolite, (b) fresh PdCl$_2$(phen)@Y, and (c–f) refer to the 1st, 5th, 10th and 16th recycled PdCl$_2$(phen)@Y, respectively.
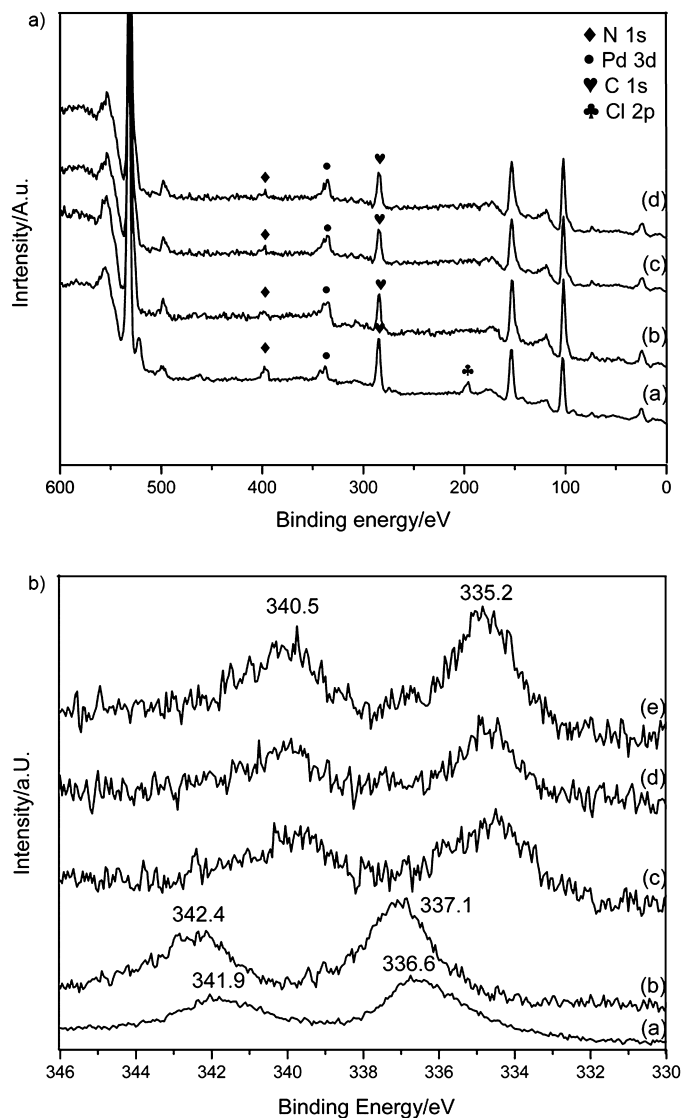

Fig. 2. XPS spectra of a) the elemental survey scan of samples: (a) fresh PdCl$_2$(phen)@Y, and (b–d) refer to the 1st, 10th and 16th recycled PdCl$_2$(phen)@Y, respectively; b) Pd 3d spectra: (a) Pd^{II}@Y, (b) fresh PdCl$_2$(phen)@Y, and (c–e) refer to the 1st, 10th and 16th recycled PdCl$_2$(phen)@Y, respectively.

342.4 eV and 337.1 eV, respectively, and were similar to the binding energies of Pd^{II}@Y [35] (Fig. 2b). Note, however, that there was a minor chemical shift of 0.5 eV for $PdCl_2$(phen)@Y, which we attribute to the difference in coordination environments between the Pd confined in the cages and of the Pd^{II}@Y construct.

The UV–vis result is consistent with FTIR spectra of the catalyst (FTIR; see Fig. S1 in Supporting information). The N_2 sorption isotherm of $PdCl_2$(phen)@Y displays the type I-like behavior of microporous materials, which indicates that the zeolite framework was not destroyed during encapsulation (N_2 sorption isotherm; see Fig. S2 in Supporting information). This result agrees with XRD patterns of the sample, which corresponds well to that of highly crystalline Y zeolite (XRD; see Fig. S3 in Supporting information). The Pd content of $PdCl_2$(phen)@Y was 2.1 wt.%, as measured by AAS. Considerable loss of surface area and pore volume was observed for the $PdCl_2$(phen)@Y construct, which is direct evidence supporting the presence of Pd complexes generally occurring inside the zeolite cages rather than on the external surface (AAS, BET and pore volume; see Table S1 in Supporting information). Thermal behaviors of the prepared [$PdCl_2$(phen)] and $PdCl_2$(phen)@Y were studied by TG and DTA in the air at 200–800 °C (TG and DTA; see Fig. S4 in Supporting information). The obvious enhancement to the thermal stability of the Pd complex caused by encapsulation, verified through a comparative thermal analysis, providing another bit of strong evidence in support of the inclusion of [$PdCl_2$(phen)] in Y zeolite.
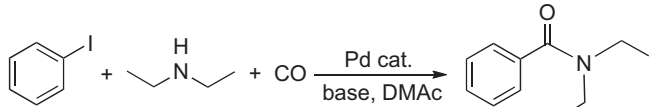
3.2. Catalytic activity

Carbonylation of aryl iodides with amines usually gives rise to mixture of mono- and dicarbonylated products [36]. Chemoselectivity of the reaction is greatly dependent on the reaction conditions [37]. Therefore, in the first stage of our study, the aminocarbonylation of iodobenzene with diethylamine was selected as a model reaction, and the influence of various reaction parameters such as bases, solvents, temperature, pressure and Pd loadings were studied (Table 1).

Previous studies had showed that bases and solvents had remarkable influences on the reactivity of the aminocarbonylation reaction [26]. To confirm the influence of bases in reaction progress, initially reaction was tried in absence of base, but no desired amides product was observed that indicates vital role of base on the reaction (Table 1, entry 1). The widely used bases for aminocarbonylation including pyridine, K_2CO_3 and Et_3N were examined and the results revealed that Et_3N or K_2CO_3 were both suitable for this reaction given 97% and 96% yields of the desired amide, respectively in comparing with poor activity of pyridine (Table 1, entries 2–4). Although K_2CO_3 and Et_3N performed almost equally well, considering of the economy of organic amines over potassium salts, Et_3N was chosen for further optimization. Notably, lowering the amount of Et_3N deteriorated the reaction rate and resulted in only 88% yield of the desired amide (Table 1, entry 5). Initial attempts to carry out the reaction in DMF as solvent resulted in a mixture of amides due to release of dimethylamine from the solvent [38,39]. Therefore, DMAc was used as a solvent and afforded unexpected fine result (Table 1, entry 4). Although other polar aprotic solvents such as N-methylpyrrolidone (NMP) demonstrated similarly superior result (Table 1, entry 6), DMAc was chosen as a solvent owing to its lower toxicity as a green solvent. On the contrary, non-polar solvent like toluene furnished lower yield of the desired product (Table 1, entry 7).

The effect of temperature on reactions was examined at 85–130 °C (Table 1, entries 4, 8 and 9). Increasing the temperature favored selectivity to the desired amides and afforded satisfactory yields without significant dehalogenation. However, in lower temperature the double carbonylation yielding the α-ketoamide

Table 1
Optimization of the aminocarbonylation reaction using heterogeneous Pd catalysts.[a]

Entry	Base	Solvent	T (°C)	P_{CO} (MPa)	Yield[b] (%)	TOF[c] (h^{-1})
1	None	DMAc	130	2	–	–
2	Pyridine	DMAc	130	2	59	84
3	K_2CO_3	DMAc	130	2	96	137
4	Et_3N	DMAc	130	2	97	139
5[d]	Et_3N	DMAc	130	2	88	126
6	Et_3N	NMP	130	2	96	137
7	Et_3N	Toluene	130	2	49	70
8[e]	Et_3N	DMAc	85	2	10	14
9[f]	Et_3N	DMAc	110	2	63	90
10	Et_3N	DMAc	130	0.5	28	40
11	Et_3N	DMAc	130	1.0	51	73
12[g]	Et_3N	DMAc	130	2	93	155
13[h]	Et_3N	DMAc	130	2	94	134
14[i]	Et_3N	DMAc	130	2	93	133

[a] Reaction conditions: $PdCl_2$(phen)@Y (0.7 mol%), PhI (10 mmol), Et_2NH (20 mmol), Et_3N (30 mmol), solvent (15 ml), 1 h.
[b] GC yield.
[c] TOF (moles of N,N-diethylbenzamide per mol of palladium per hour).
[d] Et_3N (15 mmol).
[e] Selectivity for N,N-diethylbenzamide is 23%.
[f] Selectivity for N,N-diethylbenzamide is 78%.
[g] $PdCl_2$(phen)@Y (0.2 mol%), 3 h.
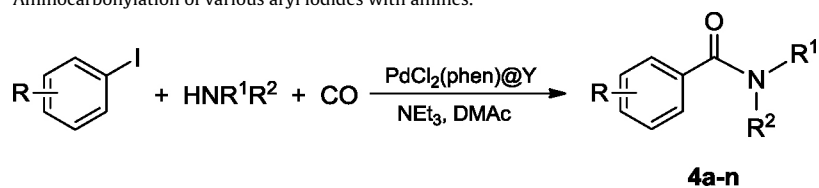[h] Pd/C (0.7 mol%).
[i] Pd/Y (0.7 mol%).

(N,N-diethyl-2-oxo-2-phenylacetamide) which was confirmed by GC–MS analysis became a significant side reaction. This result is consistent with literatures [40–42] in which reporters claimed that low temperature (60–80 °C) favored double carbonylation reactions of aryl iodide, while up to 100 °C the main products are the amides. The influence of CO pressure was also studied and the results demonstrated that increasing pressure obviously benefited the aminocarbonylation rates with improved yield and TOF of amides (Table 1, entries 4, 10 and 11). Encouraged by the high reactivity of this palladium-catalyzed system, we tried to employ a low catalyst loading. On performing the reaction with 0.2 mol% $PdCl_2$(phen)@Y resulted in 93% yield of amide and TOF of 155 h^{-1} after a prolonged reaction time to 3 h (Table 1, entry 12). Other heterogeneous catalysts like Pd/C (wt. 5%) and Pd/Y with the same Pd loadings were also investigated for the aminocarbonylation reaction and they also resulted in high yields of the desired product with 94% and 93%, respectively (Table 1, entries 13,14).

3.3. Substrate scope

Furthermore, we investigated the activity of $PdCl_2$(phen)@Y for various substrates in aminocarbonylation and the results are summarized in Table 2.
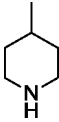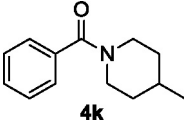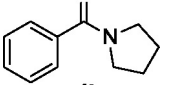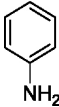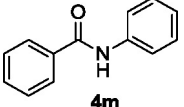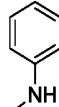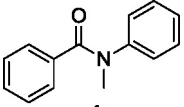
In general, various substituted aryl iodides and amines were well tolerated to afford the desired amides 4a-n in good to excellent yields. In all cases, we observed that aryl iodides consumed completely giving the desired amide products and α-ketoamide as the main byproducts. With diethylamine 2 as the amine, p-OMe, p-Me, o-Me and p-COMe substituted aryl iodides afforded high yields (93%, 90.0%, 90% and 88%, respectively) (Table 2, entries 1, 2, 4 and 5), while slightly lower yields were obtained with m-Me, p-Cl and p-NO_2 substituted aryl iodides (84%, 83% and 75%, respectively) (Table 2, entries 3, 6 and 7). It is worth noting that the TOF reached 103 h^{-1} in the case of p-iodoanisole.

Table 2
Aminocarbonylation of various aryl iodides with amines.[a]

Entry	Amine	R	Product	t (h)	Yield[b] (%)
1	(diethylamine) NH	p-OMe	4a	1.5	93
2	2	p-Me	4b	1.5	90
3	2	m-Me	4c	1.5	84
4	2	o-Me	4d	1.5	90
5	2	p-COMe	4e	1.5	88
6	2	p-Cl	4f	1.5	83
7	2	p-NO$_2$	4g	1.5	75
8	(dipropylamine) NH	H	4h	1.5	87
9	(diisopropylamine) NH	H	4i	1.5	89
10[c]	(piperidine) NH	H	4j	2	78

Table 2 (*Continued*)

Entry	Amine	R	Product	t (h)	Yield[b] (%)
11[c]	(4-methylpiperidine)	H	**4k**	2	71
12[c]	(pyrrolidine)	H	**4l**	2	73
13	(aniline, NH₂)	H	**4m**	3	85
14	(N-methylaniline, NH)	H	**4n**	3	90

[a] Reaction conditions: PdCl$_2$(phen)@Y (0.6 mol%), aryl iodide (10 mmol), amine (20 mmol), Et$_3$N (30 mmol), solvent DMAc (15 ml), 130 °C, 2 MPa.

[b] Isolated yield.

[c] 0.5 MPa.

We further tested the catalytic performances for the animocarbonylation of iodobenzene with various amines (Table 2, entries 8–14). With linear and branched aliphatic amines such as dipropylamine and diisopropylamine, the desired amides were furnished in 87% and 89% yields, respectively (Table 2, entries 8 and 9). Cyclic aliphatic amines, e.g. piperidine, 4-methylpiperdine and pyrrolidine also reacted well giving 78%, 71% and 73% yields of the corresponding amides, respectively, under relatively lower pressure (0.5 MPa) as we found higher pressure favoured the formation of α-ketoamide byproducts (Table 2, entries 10–12). PdCl$_2$(phen)@Y also showed high activity for aminocarbonylation of iodobenzene with aromatic amines, e.g., aniline and *N*-methylaniline, 85% and 90% yields, respectively were afforded although a longer time was required to complete the reaction (Table 2, entries 13 and 14).

3.4. The recycling of the catalyst

The remarkable catalytic activity of the PdCl$_2$(phen)@Y in aminocarbonylation made the results of a further study on its recycling very interesting. Recycling capacity was examined for an aminocarbonylation reaction of iodobenzene with diethylamine. The results presented in Fig. 3 showed no loss of activity in the catalyst through at least 16 reuses. Iodobenzene was totally converted each run, and the average yield of *N,N*-diethylbenzamide in consecutive reactions as promoted by the recycled catalyst approached 97% through the 1st to 16th iterations. The total TON (turnover numbers) for the 16 cycles was up to 2250. This high recyclability is very encouraging and promising from a practical application point of view.

To further understanding the underlying reason for the significant recyclability of the PdCl$_2$(phen)@Y catalyst, AAS, XPS and UV–vis were employed. Measurement of the palladium content of the catalyst after 16 consecutive runs using AAS analysis shows an extremely low level of leaching with only 0.08% of the initially added Pd lost. The XPS elemental survey scans of the fresh and recovered catalysts are almost identical, although chlorine is absent in the latter (Fig. 2a). Moreover, XPS analysis reveals that the binding energy of Pd 3d$_{5/2}$ in the recovered PdCl$_2$(phen)@Y becomes
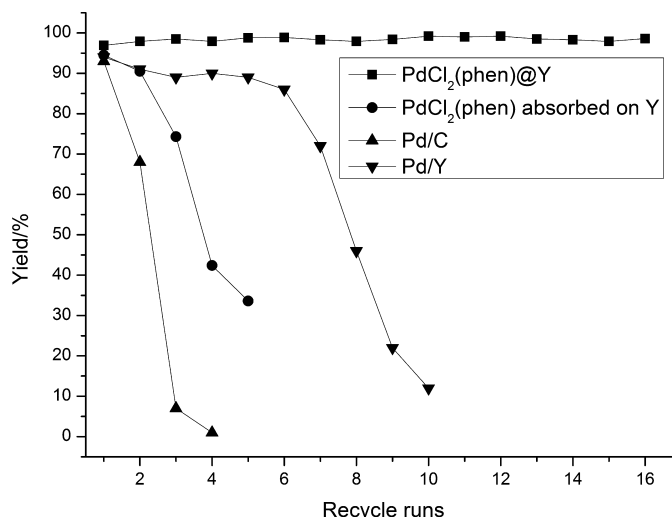

Fig. 3. Recycling tests of heterogeneous Pd catalysts. Reaction conditions: PhI (10 mmol), Et$_3$N (30 mmol), solvent DMAc (15 ml), 130 °C, CO 2 MPa, 1 h. (■) PdCl$_2$(phen)@Y (0.7 mol%), (●) [PdCl$_2$(phen)] absorbed-outside Y zeolite (0.7 mol%). (▲) Pd/C (0.7 mol%). (▼) Pd/Y (0.7 mol%).

335.2 eV (Fig. 2b). There is a remarkable decrease (1.9 eV) in Pd binding energy comparing with the fresh catalyst. These XPS results indicate that a reduction of the starting Pd^{II} complex to the lower valent state Pd^0 took place during the aminocarbonylation process. A further analysis of the UV–vis spectra of the 1st, 5th, 10th and 16th recycled PdCl$_2$(phen)@Y catalysts shows that the recycled catalysts all have the same absorption band (270 nm), which is similar to the characteristic absorption band of fresh catalyst (277 nm) (Fig. 1). The minor blue shift of the UV–vis absorption band in the recycled catalysts might result from the aforementioned reduction of the Pd^{II} complex to a Pd^0 complex [43,44]. Based on above results, we may conclude that palladium does exist inside the zeolite in a coordinated fashion with the phen ligand, and the single-molecular Pd complex could well nestle down in the supercages of the zeolite without leaching during the recycling process. 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 towards palladium, efficiently prevent the migration and leaching of the Pd complex. Thus, the Pd complexes stabilized by these Y zeolite nanocages account for the high recyclability.

For comparison, Pd/C and Pd/Y catalysts were tested for recycling under the same reaction conditions. The results, shown in Fig. 3, clearly demonstrated that both catalysts were effective in the first run of reaction. The Pd/C deactivates quickly in two or three cycles, whereas the Pd/Y could retain its high yields (>86%) of the target product in the first 6 recyclings and then gradually decayed. Compared with conventional Pd/C and Pd/Y catalysts, PdCl$_2$(phen)@Y demonstrated superior reusability and stability. This property could be attributed to a double-protection provided by the zeolitic nanocages and the strong chelation affinity of ligand for the stabilization of the active Pd species. To further prove the cooperating effect against Pd leaching, the palladium content of the reused Pd/C and Pd/Y catalysts after consecutive runs were also detected via AAS analysis. It was found that about 29% of the Pd in fresh Pd/C was leached out after the first catalytic reaction, and 80% in Pd/Y catalyst after 10 consecutive runs, compared with the negligible leaching (0.08%) in PdCl$_2$(phen)@Y after the 16 consecutive recycles. Taking into accounts the chemical state of Pd in the aminocarbonylation reaction mechanism [25,26], the Pd leaching might be due to a direct oxidative addition of aryl iodides to Pd^0 [45,46]. The PdCl$_2$(phen)@Y catalyst exhibited much lower leaching than conventional Pd/C and Pd/Y catalysts because the active Pd^0 complexes could be confined within the supercages and could not freely leach into solution. The low Pd leaching in the PdCl$_2$(phen)@Y catalyst not only reduces the cost of the catalytic process by recycling the catalyst, but also guarantees a low amount of Pd residue in the product, which is a crucial aspect in improving the product quality in practical applications.

In order to determine whether the catalysis recycle was derived from the PdCl$_2$(phen)@Y or from leaching palladium released from the solid catalyst during the reaction, we performed a hot filtration test. We focused on the aminocarbonylation reaction of iodobenzene with diethylamine. Rapid separation of the PdCl$_2$(phen)@Y catalyst by centrifugation after a 25 min reaction time (the amide yield reached 28%) and allowed the hot liquid mixture to react further 35 min under the same conditions. However, thereafter, the yield was mostly invariable which might be an evidence for a heterogeneous mechanism during the recycling. Moreover, in order to check whether the leaching amount of Pd could catalyze the aminocarbonylation reaction, we performed the reaction of iodobenzene with diethylamine in the presence of 0.0036 mol% [PdCl$_2$(phen)] as a homogeneous catalyst under the same conditions. While the amide product formation was quantitative in the heterogeneous former, in the lower concentration of homogeneous [PdCl$_2$(phen)] its formation was trace. These might indicate that the leaching of Pd could not explain the overall activity of the catalyst.

Instead of the catalyst inside the supercages performing the catalysis, the question remains as to whether it was a slowly leached catalyst owing to decomposition re-precipitated onto the surface of Y zeolite performing the catalytic recycle? To address this question, we soaked Y zeolite in a concentrated solution of [PdCl$_2$(phen)] in DMSO solution for 24 h. As the diameter of [PdCl$_2$(phen)] (~9.0 Å) is too large to effectively penetrate through the zeolite cage's free aperture (~7.4 Å) (Scheme 1), 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 with neat complex, but a different color with PdCl$_2$(phen)@Y (pink solid). However, this material deactivated quickly in two or three cycles, and failed to show any sustained catalysis (Fig. 3).

4. Conclusion

In summary, an efficient protocol for the aminocarbonylation reaction of aryl iodides with amines for synthesis of amides using [PdCl$_2$(phen)] complex encaged in Y zeolite as a highly active and reusable catalyst has been developed. The physically and chemically double-protected catalyst PdCl$_2$(phen)@Y exhibited very high conversions, with good to excellent yields and impressive recyclability during aminocarbonylation reactions, which can be easily recycled by simple filtration process up to 16 consecutive recycles without loss in activity. This significantly enhanced recyclability is due to the proposed double-protection strategy provided by the ligand and the zeolite structure for Pd^0 species generated in situ within supercages against leaching and migration. This heterogeneous catalyst has significant advantages over corresponding homogeneous catalysts, as it is not only applicable for the synthesis of a wide range of amides, but also benefits the catalyst-product separation and reduces the amount of residual palladium in the isolated products. This double-protection strategy preventing the leaching of Pd and formation of inactive Pd nanoparticles would provide an efficient and versatile way to achieve high catalytic activity and reusability, even for other Pd catalysts in carbonylation.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2014.01.010.

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