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PAPER

$PdCl_2(py)_2$ encaged in monodispersed zeolitic hollow spheres: a highly efficient and reusable catalyst for Suzuki–Miyaura cross-coupling reaction in aqueous media†

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By encaging the $PdCl_2(py)_2$ complex (py = pyridine) in the interior space of silicalite-1 hollow spheres (SHS), a novel solid palladium catalyst, $PdCl_2(py)_2$@SHS, was successfully prepared. The structure and composition of the solid catalyst was characterized by SEM, TEM, XRD, N_2 sorption, FT-IR and XPS. This catalyst afforded fast conversions for the Suzuki–Miyaura cross-coupling reactions of various aryl halides and arylboronic acids even at Pd loadings of 0.0188 mol% in aqueous media. The turnover frequency (TOF) could be up to 63 210 h^{-1} under mild conditions in air. In particular, because of the antileaching effect of the surrounding zeolitic shell toward the entrapped Pd species, $PdCl_2(py)_2$@SHS showed outstanding stability and reusability, which could be reused at least 10 times without appreciable loss of its activity. The developed solid catalyst combined with the mild conditions represented one of the most efficient heterogeneous systems for the Suzuki–Miyaura cross-coupling reactions of aryl halides.

Introduction

The Suzuki–Miyaura cross-coupling reaction, which is unique, requiring mild reaction conditions and showing a high degree of tolerance for a variety of functional groups, has become unarguably one of the most powerful synthetic methods for preparing biaryl compounds, such as natural products, pharmaceuticals, and polymers, *etc.*[1] Because of the great significance of this reaction, it was recognized by awarding the 2010 Nobel Prize in Chemistry.[2] Most applications of the reaction involve homogeneous catalysts consisting of palladium complexes with a variety of ligands.[3] These catalytic systems generally exhibit better activity and selectivity than heterogeneous systems, however, they suffer from the practical problems such as catalyst separation and recycling. To solve these problems and make the process more green, researchers have immobilized palladium complexes on various supports such as carbon,[4] magnetic materials,[5] silica,[6] hydroxyapatite,[7] zeolites,[8] MOFs[9] and organic polymers[10] to create heterogeneous catalysts. Consequently, achieving a combination of the advantages of both the homogeneous and the heterogeneous processes is always the focus in catalysis.[1k,11]

Among various shell materials, zeolitic shell hollow spheres have been demonstrated extraordinarily to be a nontoxic, highly biocompatible, and hydrothermal/mechanically stable material, so they have many practical applications in the areas as diverse as biological chemistry, synthesis, photonics, and catalysis.[12] These spheres act as bi-functional systems for catalysis applications where the access to the interior of the particles having the active components is controlled by the zeolitic micropores on the shell. However, over the past decade, most of the research efforts have been focused only on hollow spheres as the support of noble metal nanoparticle catalysts for heterogeneous catalysis.[13] So far, there are few reports on hollow spheres as "containers" for homogeneous catalysts, especially noble metal complexes.

Another concern in such reactions, is the complete or at least partial replacement of organic solvents by environmental benign reaction media.[3d,14] We wish to report herein our preliminary result to develop a more active and reusable heterogeneous palladium complex catalyst for Suzuki–Miyaura cross-coupling reactions under mild and environmental friendly conditions. A novel and non-phosphine catalyst, $PdCl_2(py)_2$ (py = pyridine) encaged in the interior space of silicalite-1 hollow spheres (SHS), $PdCl_2(py)_2$@SHS, was successfully prepared through a "ship-in-bottle" method.[15] This microcapsular reactor afforded fast conversions for the Suzuki–Miyaura cross-coupling reactions of various aryl halides and arylboronic acids even at catalyst loadings of 0.0188 mol%. The turnover frequency (TOF) could be up to 63 210 h^{-1} under mild conditions in air. Investigations on the reusability and stability of the heterogeneous palladium

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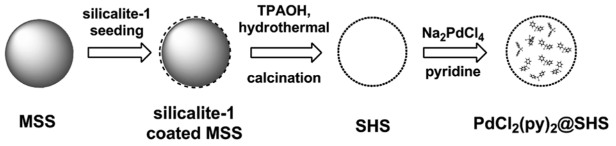
† Electronic supplementary information (ESI) available: Experimental details and instrumentation of the synthesis of SHS, SEM images of MSS, silicalite-1 seeds, silicalite-1 coated MSS and shell-crushed $PdCl_2(py)_2$@SHS, ^1H NMR data. See DOI: 10.1039/c2gc35302d



Scheme 1 Preparation of the microcapsular reactor, $PdCl_2(py)_2$@SHS.

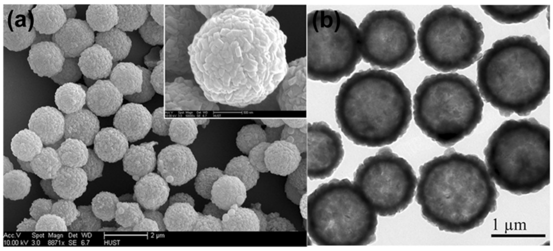


Fig. 1 (a) SEM and (b) TEM images of $PdCl_2(py)_2$@SHS. The inset in (a) is the SEM image at high magnification to depict the zeolite lattice fringes.

catalyst were also discussed herein. To the best of our knowledge, this is the first example of employing silicalite-1 hollow spheres as "containers" for palladium complexes in Suzuki–Miyaura cross-coupling reactions.

Results and discussion

Catalyst preparation and characterization

As illustrated in Scheme 1, silicalite-1 hollow spheres (SHS) are fabricated *via* a layer-by-layer technique and a two-step hydrothermal treatment.[16] By means of *in situ* synthesis, $PdCl_2$ and pyridine are introduced into the interior space of SHS by batch equilibrium technique successively. The white powder turns into brown firstly, then light yellow. After washing with solvent thoroughly and drying, the solid remains white. The Pd content of the $PdCl_2(py)_2$@SHS catalyst is 0.10 wt% measured by atomic absorption spectroscopy (AAS). The N and C contents of the $PdCl_2(py)_2$@SHS catalyst determined by combustion chemical analysis are 0.03 wt% and 0.11 wt%, respectively. The atom ratios of Pd, N and C (1 : 2.1 : 9.5) on the solid catalyst fall into a good agreement with the ratios expected ($PdCl_2(py)_2$, $C_{10}H_{10}N_2PdCl_2$).

Fig. 1a depicts the scanning electron microscopy (SEM) images of the $PdCl_2(py)_2$@SHS catalyst, the catalyst presents with a monodispersed, uniform spherical morphology with the coarse outer surface composed of closely packed silicalite-1 nanocrystals. The particle diameter is ranging from 1.0 to 1.2 μm. The zeolite lattice fringes observed in the image (inset of Fig. 1a) at high magnification extend through the entire crystals, also manifesting that the capsular shells are, indeed, composed of silicalite-1 nanocrystals. The hollow structures of the spheres are proved by transmission electron microscopy (TEM) (Fig. 1b). The hollow interior diameter is nearly 1.0 μm and the thickness of shell is about 200 nm.

The XRD patterns of silicalite-1, SHS and $PdCl_2(py)_2$@SHS are shown in Fig. 2. The characteristic diffraction peaks assign to the silicalite-1 zeolite consistently, confirming the MFI structure of the shell,[17] which gives no evidence for another crystalline phase. The N_2 sorption isotherm of $PdCl_2(py)_2$@SHS (Fig. 3) displays a type I like behavior of microporous materials. The BJH pore size distribution of $PdCl_2(py)_2$@SHS (inset of Fig. 3) shows a sharp peak at 0.56 nm which is in agreement with the microporous dimension of silicalite-1 zeolite.[18] These results further confirm the shells of $PdCl_2(py)_2$@SHS are composed of silicalite-1.

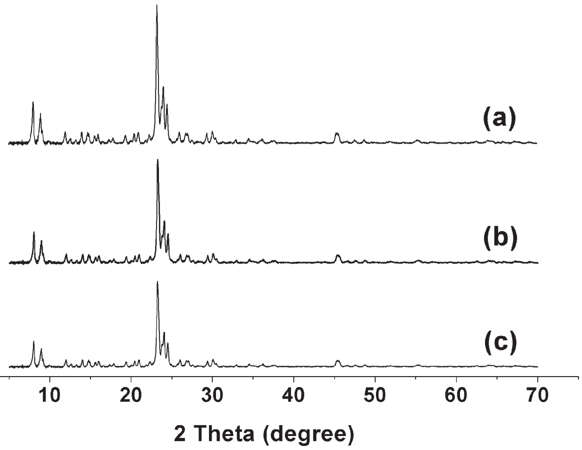


Fig. 2 XRD patterns: (a) silicalite-1; (b) SHS; (c) $PdCl_2(py)_2$@SHS.

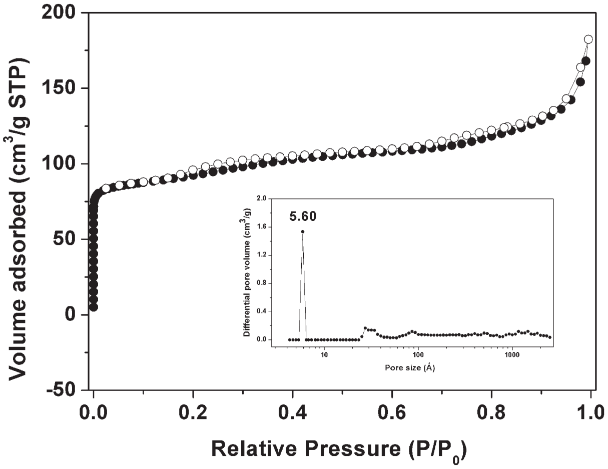


Fig. 3 N_2 sorption isotherm of $PdCl_2(py)_2$@SHS. The inset is the corresponding pore size distribution.

The FT-IR spectra of $PdCl_2(py)_2$, SHS and $PdCl_2(py)_2$@SHS catalyst are shown in Fig. 4 in the 400–4000 cm^{-1} region. As can be seen, both the SHS and $PdCl_2(py)_2$@SHS exhibit the band typical of 550 cm^{-1}, which confirms that the sample possesses a MFI type framework, and the intensity ratio of 550 to 450 cm^{-1} is indicative of the high crystallinity of the product.[19] Compared with pure SHS, $PdCl_2(py)_2$ and $PdCl_2(py)_2$@SHS show characteristic adsorptions at 1602.6 cm^{-1} and 1448.3 cm^{-1} in both cases attributed to the stretching vibrations of the C═N and C═C double bonds. Furthermore, the characteristic adsorption peaks at 694.6 cm^{-1} is assigned to the deformation vibrations of the═C–H bonds. These results indicate the existence of the palladium complex, $PdCl_2(py)_2$ in the catalyst.

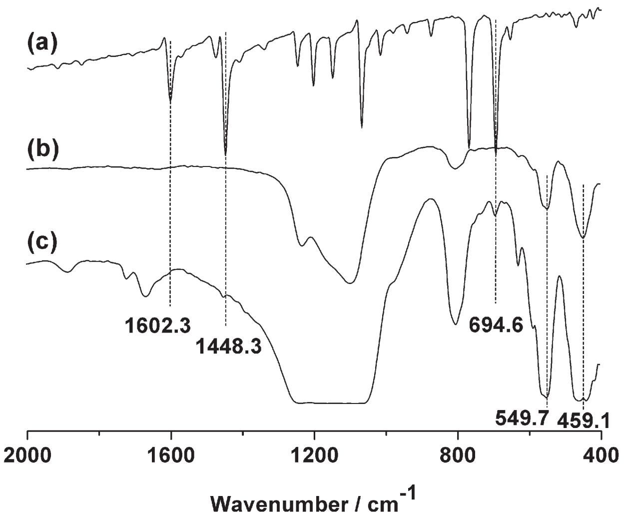


Fig. 4 FT-IR spectra: (a) $PdCl_2(py)_2$; (b) SHS; (c) $PdCl_2(py)_2$@SHS.

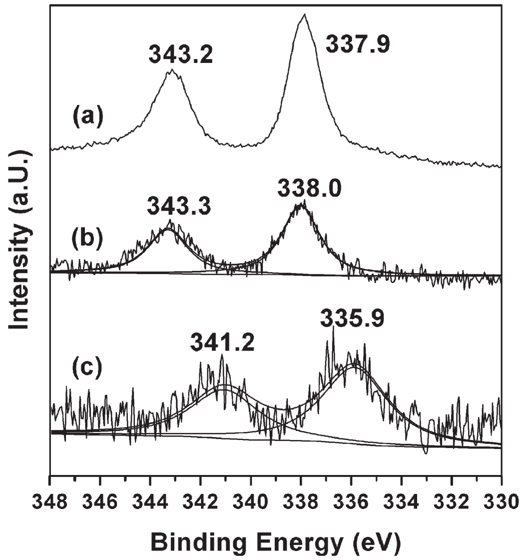
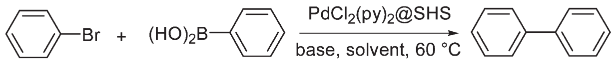


Fig. 5 XPS Pd 3d spectra: (a) $PdCl_2(py)_2$; (b) $PdCl_2(py)_2$@SHS; (c) 10th recycled $PdCl_2(py)_2$@SHS. All the samples were heavily ground to expose the Pd species before XPS characterization (see ESI, Fig. S5†).

In order to obtain an insight into the oxidation state and coordination environment of palladium in the $PdCl_2(py)_2$@SHS catalyst, X-ray photoelectron spectroscopy (XPS) experiments were performed. Fig. 5 displays the Pd binding energy of $PdCl_2(py)_2$ and $PdCl_2(py)_2$@SHS. $PdCl_2(py)_2$@SHS exhibits two observable peaks centered at 343.3 and 338.0 eV, which are assigned to Pd $3d_{3/2}$ and Pd $3d_{5/2}$, respectively.[20] This result is the same with $PdCl_2(py)_2$ complex and implies that the oxidation state of Pd is +2 and also a coordination interaction between Pd and pyridine might be involved. The above characterization experiments confirm that the Pd complex, $PdCl_2(py)_2$ is successfully encaged in the SHS, the schematic model of the $PdCl_2(py)_2$@SHS catalyst proposed in Scheme 1 should be reasonable.

Table 1 The effect of solvents and bases[a]



Entry	Solvent	Base	Time (min)	Yield (%)[b]
1	MeOH	K_2CO_3	60	5
2	DMF–H_2O (10 : 1)	K_2CO_3	60	9
3	H_2O	K_2CO_3	60	24
4	EtOH	K_2CO_3	60	23
5	EtOH–H_2O (1 : 2)	K_2CO_3	60	40
6	EtOH–H_2O (1 : 1)	K_2CO_3	60	56
7	EtOH–H_2O (3 : 2)	K_2CO_3	60	78
8	EtOH–H_2O (3 : 2)	Na_2CO_3	60	69
9	EtOH–H_2O (3 : 2)	$NaHCO_3$	60	62
10	EtOH–H_2O (3 : 2)	NaOAc·3H_2O	60	70
11	EtOH–H_2O (3 : 2)	KOAc	60	71
12	EtOH–H_2O (3 : 2)	Na_3PO_4·12H_2O	60	85
13	EtOH–H_2O (3 : 2)	K_3PO_4·3H_2O	60	99 (97)[c]
14	H_2O	K_3PO_4·3H_2O	60	53
15	EtOH–H_2O (3 : 2)	K_3PO_4·3H_2O	10	99 (96)[c]
16	EtOH–H_2O (3 : 2)	K_3PO_4·3H_2O	20	90[d]

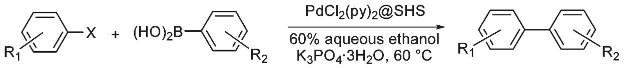
[a] Reaction conditions: 10 mg of $PdCl_2(py)_2$@SHS (0.0188 mol% of Pd), 0.5 mmol of bromobenzene, 0.75 mmol of phenylboronic acid, 1 mmol of base, 2 ml of solvent (v/v), 60 °C in air. [b] GC yield (naphthaline as internal standard). [c] Isolated yield in parentheses. [d] 10 mmol scale.

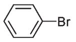
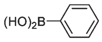
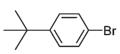
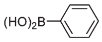
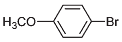
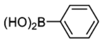
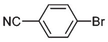
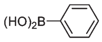
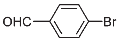
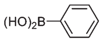
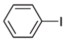
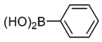
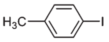
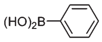
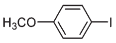
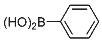
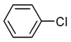
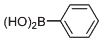
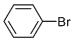
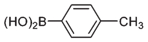
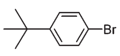
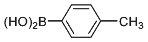
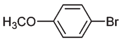
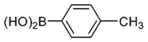
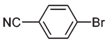
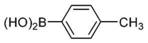
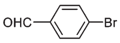
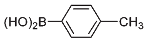
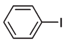
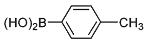
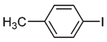
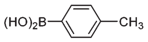
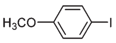
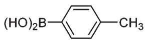
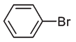
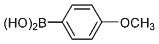
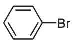
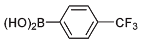
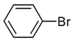
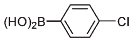
The Suzuki–Miyaura cross-coupling reaction

We first tested the catalytic activity of $PdCl_2(py)_2$@SHS in the Suzuki–Miyaura cross-coupling reaction between bromobenzene and phenylboronic acid, and the results are summarized in Table 1. Previous studies have showed that solvents and bases had remarkable influences on the reactivity of the Suzuki reaction.[3d,6d,21] Our interest is using water to replace organic solvents in such reaction because water solvent endows the reaction with green and safe properties.[14] In addition, the hydrophilic nature of the microporous silica can induce a wettability control over the catalytic reactions in aqueous media. Hydrophilic liquids may be preferentially adsorbed into the composite microcapsular reactor. Our preliminary screening of solvent revealed that the presence of ethanol could efficiently promote the Suzuki–Miyaura reaction in water. And the optimal condition when using K_2CO_3 as base, 60% aqueous ethanol was the best choice for the reaction medium (Table 1, entries 1–7). Under the same conditions, Na_2CO_3, $NaHCO_3$, NaOAc·3H_2O and KOAc gave moderate biphenyl yields (Table 1, entries 8–11). Remarkably, when Na_3PO_4·12H_2O and K_3PO_4·3H_2O were used (Table 1, entries 12 and 13), good to excellent biphenyl yields were obtained, while K_3PO_4·3H_2O in pure water only gave 53% of biphenyl (Table 1, entry 14). Indeed, K_3PO_4·3H_2O in 60% aqueous ethanol was found to be the best choice in view of almost quantitative biphenyl yield obtained within a considerably short reaction time (10 min) (Table 1, entry 15). A reaction in 10 mmol scale was also carried out, and it was found that the reaction proceeded uneventfully, indicating the effectiveness of this catalyst for practical synthesis (Table 1, entry 16).

With the optimized solvent and base in hand, we investigated the activity of $PdCl_2(py)_2$@SHS for various substrates. All the reactions were carried out at 60 °C in air using K_3PO_4·3H_2O as

Table 2 Suzuki–Miyaura cross-coupling catalyzed by $PdCl_2(py)_2$@SHS[a]



Entry	ArX	ArB(OH)$_2$	Time (min)	Yield (%)[b]	TOF (h^{-1})[c]
1			10	97	30 970
2			15	97	20 650
3			20	88	14 050
4			5	99	63 210
5			35	99	9120
6			10	96	30 650
7			10	92	29 370
8			15	99	21 070
9			60	7	275
10			5	96	61 300
11			15	98	20 860
12			15	94	20 010
13			5	99	63 210
14			35	98	8940
15			5	99	63 210
16			10	99	31 610
17			15	94	20 010
18			15	86	18 300
19			20	83	13 250
20			15	88	18 730

[a] Reaction conditions: 10 mg of $PdCl_2(py)_2$@SHS (0.0188 mol% of Pd), 0.5 mmol of aryl halide, 0.75 mmol of arylboronic acid, 1 mmol of $K_3PO_4{\cdot}3H_2O$, 2 ml of EtOH : H_2O (3 : 2 v/v), 60 °C in air. [b] Isolated yield. [c] mol biaryl/mol Pd h.

base and 60% aqueous ethanol solution as reaction medium. The results are summarized in Table 2. At the Pd loading of 0.0188 mol%, $PdCl_2(py)_2$@SHS afforded satisfactory biaryl yields (88–99%) for aryl bromides containing –*t*-Bu, –OCH_3, –CN and –CHO groups within 5 min–35 min (Table 2, entries 2–5). It is worth noting that the TOF reached *ca.* 63 210 h^{-1} in the case of 4-cyanobromobenzene. For iodobenzene and other aryl iodides with substituents such as –CH_3 and –OCH_3, complete conversions were observed and the corresponding biaryl products in 92–99% yields were also achieved within 10 min–15 min (Table 2, entries 6–8). Further study indicated that chlorobenzene can also react with phenylboronic acid. However, the yield of biphenyl was very poor (7%) even prolonged the reaction time (60 min) (Table 2, entry 9). $PdCl_2(py)_2$@SHS also showed a high activity for the Suzuki–Miyaura cross-couplings of 4-methylphenylboronic acid, satisfactory yields could be also obtained within 5 min–35 min (Table 2, entries 10–17). For 4-cyanobromobenzene and iodobenzene, the TOF also reached *ca.* 63 210 h^{-1}. We further tested the catalytic performances for the couplings of various arylboronic acids with bromobenzene (Table 2, entry 18–20). For arylboronic acids bearing electron-donating group –OCH_3 and electron-withdrawing groups –CF_3 and –Cl, 86%, 83% and 88% yields were obtained, respectively.

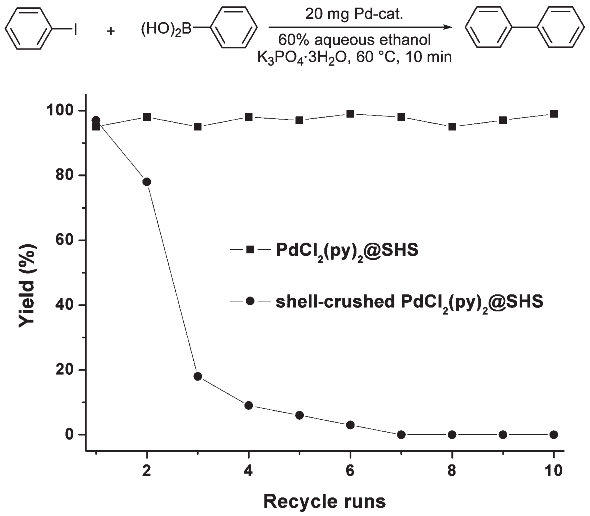


Fig. 6 Recycling test of $PdCl_2(py)_2$@SHS before and after shell-crushed by heavily grinding.

In order to determine whether the catalysis was derived from the $PdCl_2(py)_2$@SHS or from leaching palladium, which is released from the SHS hollow spheres during the reaction and then re-absorbed to the SHS at the end, we performed a hot filtration test.[22] We focused on the Suzuki–Miyaura cross-coupling reaction of 4-bromobenzaldehyde with phenylboronic acid. Rapid separation of the $PdCl_2(py)_2$@SHS catalyst by centrifugation after a 15 min reaction time (the conversion of 4-bromobenzaldehyde reached 63%) and allowed the hot liquid mixture to react further. We found that no further reaction was observed and no palladium could be detected in the hot liquid mixture by AAS. This result demonstrates that the palladium catalyst remains inside the SHS during the reaction.

The recyclability of $PdCl_2(py)_2$@SHS was also investigated with consecutive Suzuki–Miyaura cross-coupling reactions of iodobenzene with phenylboronic acid (Fig. 6). This catalyst could be recycled 10 times without any loss of activity. The average yield of biphenyl in consecutive reactions promoted by the 1st through to the 10th recycled catalyst was up to 97% and the total TON (turnover numbers) for 10 cycles was up to 25 800. Undoubtedly, this result is very promising and encouraging from a practical point of view.[1j,k] For comparison, shell-crushed $PdCl_2(py)_2$@SHS was also investigated. As expected, it deactivated quickly in two or three cycles. Furthermore, according to the SEM and TEM images shown in Fig. 7, the used $PdCl_2(py)_2$@SHS spheres can retain their dense zeolitic shell even after 10 recycles, indicating a good stability of $PdCl_2(py)_2$@SHS in liquid reaction. The palladium content of the catalyst was determined by AAS after ten consecutive runs and no appreciable change was observed. XPS analysis revealed the binding energy of Pd $3d_{5/2}$ in the 10th recycled catalyst was 335.9 eV (Fig. 5c). The remarkable decrease (2.1 eV) in Pd binding energy was observed comparing with the fresh catalyst. This result indicated that the reduction of the starting palladium(II) complex to the lower valent state Pd(0) had taken place during the Suzuki–Miyaura cross-coupling reaction.[23]

To further confirm the Pd species were effectively entrapped inside the intact zeolitic shell in our $PdCl_2(py)_2$@SHS catalyst, we employed a mixture of iodobenzene and sterically hindered 5-iodo-*m*-xylene as the substrates, 98% of biphenyl, and 3% of 3,5-dimethylbiphenyl were obtained by coupling with phenylboronic acid (Scheme 2). The size of 5-iodo-*m*-xylene is too large to permeate into the zeolitic shell and can not be successfully converted on the encaged Pd species consequently. On the contrary, after the zeolitic shell was destroyed by heavy grinding (see ESI, Fig. S5†), the shell-crushed $PdCl_2(py)_2$@SHS displayed a very high product yields of both biphenyl and 3,5-dimethylbiphenyl within 10 min (97% and 95%, respectively). Similarly, for an isomeric mixture system of methyl 4-iodobenzoate and methyl 2-iodobenzoate, the $PdCl_2(py)_2$@SHS catalyst gave 92% of 4-methoxycarbonylbiphenyl and only 5% of 2-methoxycarbonylbiphenyl, while the shell-crushed catalyst gave 93% and 89%, respectively. Extraordinarily, the superior substrate selectivity of the $PdCl_2(py)_2$@SHS catalyst in both sterically hindered and isomeric systems originated from the shape-selectivity of the zeolitic shell, allowing it to find practical applications in some mixture separation-inextricable organic synthesis.

Indeed, each of the spheres is a true micrometer-sized reactor with active ingredients entrapped in the hollow space surrounded by a zeolitic shell of *ca.* 200 nm. The uniform microporous channels on the shell have a dimension of about 0.56 × 0.53 nm (*i.e.*, the microporous dimension of silicalite-1 zeolite)[18] and provide entrances for the reactants, exits for the products as well as protection for $PdCl_2(py)_2$ complex from leaching. Furthermore, the interior space (diameter 1 μm) is large enough to accommodate a desired number of metal complexes in a confined space; and the catalytic complexes can wander freely since there are no covalent linkages or other strong interactions between the complexes and the internal surface of silicalite-1 hollow spheres (SHS). Consequently, the $PdCl_2(py)_2$ can be trapped within the micrometer-sized hollow interior space to form an unique encaged microenvironment for the reaction as the homogeneous catalyst. On the other hand, the whole catalyst apparently behaves just like a heterogeneous catalyst, which can be recovered and reused easily in virtue of the high thermal/chemical stability of the zeolitic shell.

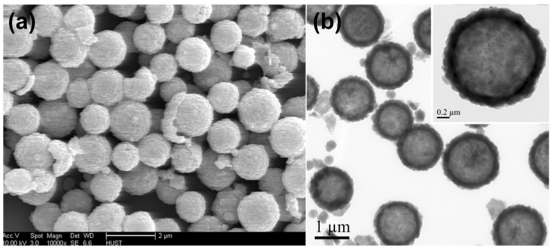


Fig. 7 (a) SEM; (b) TEM images of 10th recycled $PdCl_2(py)_2$@SHS. The inset in (b) is the TEM image at high magnification.

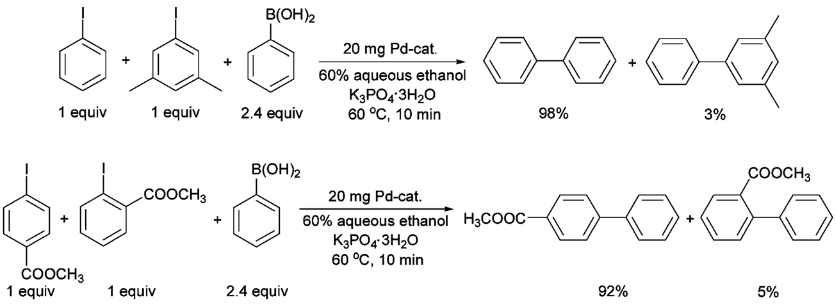
Conclusions

By encaging the $PdCl_2(py)_2$ complex in the interior space of silicalite-1 hollow spheres (SHS), a novel and non-phosphine solid palladium catalyst, $PdCl_2(py)_2$@SHS, was successfully prepared. This catalyst afforded fast conversions for the Suzuki–Miyaura cross-coupling reactions of various aryl halides and arylboronic acids even at catalyst loadings of 0.0188 mol%. The turnover frequency (TOF) could be up to 63 210 h^{-1} under mild conditions in air. In particular, because of the antileaching effect of the surrounding zeolitic shell toward the entrapped Pd species, $PdCl_2(py)_2$@SHS shows outstanding stability and reusability, can be reused at least 10 times without any activity decrease. In addition, the developed solid catalyst exhibits superior substrate selectivity in a mixed system for practical synthesis.

Experimental

Reagents and materials

n-Hexadecylamine, tetrapropylammonium hydroxide (TPAOH, 1 M in water), aryl halides were purchased from Alfa Aeser, palladium chloride ($PdCl_2$), pyridine (py), naphthalene, $K_3PO_4 \cdot 3H_2O$ and other bases, polydiallyldimethyl ammonium chloride (PDDA, M_w = 160 000, 40 wt% in water), poly(sodium 4-styrene sulfonate) (PSS, M_w = 200 000, 20 wt% in water), tetraethoxyorthosilane (TEOS) were commercially available. All



Scheme 2 $PdCl_2(py)_2$@SHS for mixed system.

chemicals were used without further purification. The syntheses of mesoporous silica spheres (MSS) and silicalite-1 seeds were expatiated in the ESI.†

Synthesis of silicalite-1 hollow spheres (SHS)

Silicalite-1 hollow spheres were fabricated according to the literature,[16] with some modifications. The silicalite-1 coated MSS were treated through a two-step hydrothermal approach: 0.1 g of silicalite-1 coated MSS were hydrothermally treated in 15 ml of 1.5 wt% TPAOH aqueous solution at 100 °C for 1 h, and then continuously treated in 15 ml aqueous solution with a molar composition of TPAOH : TEOS : H_2O = 3 : 10 : 2000 at 100 °C for 8 h. The solid product was separated by centrifugation and washed with distilled water three times. After drying at 60 °C for 2 h, templates in the samples were removed by calcination in air at 550 °C for 4 h.

Loading of $PdCl_2(py)_2$ complex into SHS

The introduction of $PdCl_2(py)_2$ complex into hollow spheres was performed by using batch equilibrium technique. Firstly, 0.1 g of hollow spheres was immersed into 2 ml of Na_2PdCl_4 aqueous solution with initial concentrations of 0.5 M. Then they were left for 24 h at room temperature in order to reach the concentration equilibrium. Upon equilibration, the solid products were recovered by centrifugation. After drying in vacuum over night, a light brown solid was obtained, and then 2 ml pyridine in acetone was added. The mixture was left for 24 h at room temperature. Finally, the light yellow solid was separated by centrifugation, washed with water, DMF and acetone thoroughly in sequence, then Soxhlet extraction with acetone for 48 h was also employed to make sure no Pd^{2+} and Pd complex adhered to the outside of the hollow spheres. A white solid was obtained after drying at 60 °C under vacuum overnight and denoted as $PdCl_2(py)_2$@SHS.

Catalytic activity test and recycling

All reactions were conducted in a 10 mL tubular flask equipped with a magnetic stirring bar. In a typical procedure, 10 mg $PdCl_2(py)_2$@SHS, 0.5 mmol bromobenzene, 0.75 mmol phenylboronic acid and 1 mmol $K_3PO_4 \cdot 3H_2O$ were added to 2 ml solvent (EtOH : H_2O = 3 : 2 v/v). The mixture was stirred at 60 °C in air for 10 min. The product was obtained by preparative TLC using petroleum ether (bp 60–90 °C) as the eluting solvent. Particularly, for the 4-cyanbiphenyl, a mixed solution of ethyl acetate and petroleum ether (1 : 10, v/v) was used. The product was confirmed by ^1H NMR.

For the recycling experiments, 20 mg $PdCl_2(py)_2$@SHS, 0.5 mmol iodobenzene, 0.75 mmol phenylboronic acid, 1 mmol $K_3PO_4 \cdot 3H_2O$, and 50 mg naphthaline (as internal standard for GC analysis) were added to 2 ml solvent (EtOH : H_2O = 3 : 2 v/v). The reaction was carried out at 60 °C in air for 10 min. Then the mixture was separated quickly by centrifugation. The clear supernatant was analyzed by GC. The obtained catalyst was washed by distilled water and ethanol, dried under vacuum and used in the next run.

Characterization and analysis

N_2 physical adsorption was carried out on a Micrometrics ASAP 2020 M volumetric adsorption analyzer (before the measurements, samples were degassed at 383 K for 8 h under 10^{-5} bar vacuum). The Brunauer–Emmett–Teller (BET) surface area was evaluated from data in the relative pressure range from 0.05 to 0.25. The total pore volume of each sample was estimated from the amount adsorbed at the highest P/P_0 (above 0.99). Pore diameters were determined from the adsorption branch using Barrett–Joyner–Halenda (BJH) method. Scanning electron microscopy (SEM) images were obtained on a FEI Sirion 200 scanning electron microscope at 10.0 kV. Transmission electron microscopy (TEM) was carried out on a FEI Tecnai G2 20 electron microscope running at 200 kV. The XRD patterns were obtained on a Bruker Advanced D8 diffractometer over a 2θ range of 5°–70° with Cu Kα radiation. Pd content was analyzed by atomic absorption spectrometry (AAS) on a Perkin Elmer AA-300. The C, N elemental analyses were carried out on a Vario Micro cube Elemental Analyzer. FT-IR spectra in KBr pellet were collected on Bruker Equinox 55 FT-IR spectrophotometer in the range 4000–400 cm^{-1}. The XPS analysis was carried out with a VG Multilab 2000 spectrometer using Al Kα radiation at a power of 300 W. The pass energy was set at 100 eV, and C_{1s} line at 284.6 eV was used as a reference. All the samples were washed with acetone, dried and heavily ground to expose the Pd species before XPS characterization. The products of the coupling reaction were identified by ^1H NMR spectra using a 400 MHz Bruker AV400 instrument in $CDCl_3$. Chemical shifts are reported in parts per million (ppm) downfield from TMS. The ^1H NMR spectra of biaryls and the melting points of solid biaryls were in accordance with literature reports. GC analyses were performed in a Fuli GC9790, equiped with a FFAP (30 m × 0.25 mm × 0.25 μm) capillary column and a flame ionization detector (FID).

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