

# Heck coupling in zeolitic microcapsular reactor: A test for engaged quasi-homogeneous catalysis

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## Abstract

A new strategy of heterogenizing homogeneous catalysts by engaging the quasi-homogeneous catalytic reaction into a zeolitic microcapsular reactor has been proposed. As an example toward achieving such goal, a highly stable, nanopalladium-entrapped zeolitic microcapsular reactor (Pd@S1) was successfully fabricated and evaluated for Heck coupling reaction. The Pd@S1 not only exhibits excellent reactivity at low Pd adoption (Pd/PhI = 0.0025) during the reaction, but also can be reused for more than 10 runs with negligible loss of activity, in contrast to rapid decay of activity of conventional Pd/C catalysts. Such reusability can be explained by the encapsulation of the “quasi-homogeneous” reaction mechanism of Heck coupling within the micrometer-sized hollow cavities of Pd@S1, which successfully avoids the Pd leaching during the reaction. The strategy may be helpful in the design of reusable, highly efficient catalysts with advantages deriving from both homogeneous and heterogeneous catalysts.

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**Keywords:** Zeolitic microcapsular reactor; Heck coupling; Catalysis; Palladium; Leaching; Recycle

## 1. Introduction

Homogeneous and heterogeneous catalysis are two main types of industrial catalytic processes. The former has a high catalytic efficiency but also has difficulty separating the used catalyst from the product after the reaction. Adopting a heterogeneous catalyst could solve the problem of catalyst recovery and reuse, but in most cases, the catalyst's low utility and the complexity of the reaction mechanism become new problems in its application. Consequently, achieving a combination of the advantages of both the homogeneous and heterogeneous processes is always the focus in catalysis [1,2]. The Heck coupling reaction is considered important in such explorations, not only for its significance in C–C coupling reaction between aryl halides and olefins [3–5], but also for its characteristic “quasi-homogeneous” reaction mechanism [6–10]. Up to now, many types of homogeneous catalysts have been used for this reaction, including palladium acetate [11], palladacy-

cles [12], and palladium complexes liganded with phosphine [13] or carbene [14]. Meanwhile, many groups are exploring various heterogeneous catalysts, such as ligand-protected palladium nanoparticles [15,16], palladium on active carbon (Pd/C) [17–19] or carbon nanotubes [20], palladium on porous inorganic supports [21–26] or functionalized polymers [27,28], and zeolite-immobilized palladium species [29–34]. Although some have claimed that their catalysts can be recycled to some extent for the redeposition of Pd, the leaching of the palladium species from the catalyst [6,8,9,28] is still considered the main problem during its heterogenized process because of the quasi-homogeneous mechanism of Heck coupling via a soluble intermediate of the solvated Pd clusters or even palladium complex [Pd(II)(ArX)(solvent)(base)] [6–10], especially in the systems using highly active aryl iodides as substrates and highly efficient aprotic polar reagents (e.g., *N*-methylpyrrolidone [NMP] or *N,N*-dimethylacetamide) as solvents. Recently, de Vries and co-workers [9,35–38] developed a new strategy to enhance the efficiency of Heck coupling reaction by adopting the homeopathic palladium as the catalyst. Because very little amount of Pd (0.01–0.1 mol% of the amount of the substrate) is used in

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the reaction, further recycling of the catalyst is not necessary. However, a longer reaction time seems to be needed to reach the high product yield.

In another important route to solving the problem, some deliberately designed reaction conditions and/or catalysts to enhance the catalyst's reusability, such as introducing an additional inorganic base [7], modifying the support with functional groups (e.g., amino-, thiol-) [28,39–41], or performing the reaction in an unusual solvent (e.g., molten tetralkylammonium salts [42], polyethyleneglycol [43]), have been adopted. One of the most interesting examples in this field is the commercial catalyst [PdEnCat], in which the active palladium species are protected by a matrix of cross-linked porous polyurea containing heteroatom in its backbone [44–46]. However, the literature and our recent work found that its organic moiety bears the poor thermal stability and tends to be dissolved in the aprotic polar solvents [47,48]. Further studies on the reaction progress of such catalyst have revealed that the palladium actually leaches into the reaction solution to participate the reaction and redeposits back onto the support after completion of the reaction [49–51]. In this work, a new strategy was proposed to engage the entire quasi-homogeneous catalytic process into an inorganic microcapsular reactor with a zeolitic shell to realize the heterogenized homogeneous reaction. The nanopalladium-entrapped zeolitic microcapsular reactor (Pd@S1) was fabricated as the first successful achievement of such strategy and was further evaluated as the catalyst for Heck coupling reaction. Because of the uniform microporosity and high thermal/chemical stability of the zeolitic shell, the in situ formed active species [Pd(II)(ArI)(solvent)(base)] or solvated Pd-clusters during the reaction can be trapped within the micrometer-sized hollow core of zeolitic capsules to form a unique engaged microenvironment for the homogeneous catalysis. On the other hand, the whole catalyst apparently behaves just like a heterogeneous catalyst, which can be recovered and reused facilely.

## 2. Experimental

### 2.1. Materials

3-amino-propyltriethoxysilane (APS), palladium(II) acetylacetonate, dodecane, 4-iodotoluene, 2-iodothiophene, 5-iodo-*m*-xylene, and benzothiazole (98%) were purchased from Aldrich. The 5 wt% Pd/C was supplied from Shanghai July Chemical Company. *N*-methyl-2-pyrrolidone (NMP), cyclohexane, potassium borohydride (KBH<sub>4</sub>, 94 wt%), tetrapropylammonium hydroxide (TPAOH, 25 wt% in water), tetraethoxyorthosilane (TEOS), ethanol (EtOH), styrene, iodobenzene and methyl acrylate were obtained from Shanghai Chemical Reagent Company. All chemicals were used without further purification.

### 2.2. Catalyst preparation

The Pd@S1 catalyst was synthesized according to the liquid-phase transformation of nanozeolite-seeded, Pd-preincorporat-

ed mesoporous silica spheres (MSSs), as described in our previous reports [52–55]. The MSS template was synthesized according to the procedure reported by Unger et al. [56]. After surface NH<sub>2</sub> modification with APS at room temperature [57] to enhance the immobilization capability toward Pd species, the MSSs were impregnated in 0.04 M ethanolic solution of palladium(II) acetylacetonate under stirring at ambient temperature for 30 min. Then the Pd(II) species loaded in the MSSs were further transformed into Pd nanoparticles via in situ reduction in a 0.01 M KBH<sub>4</sub> aqueous solution and calcinations in air at 600 °C for 3 h.

To obtain the target Pd-trapped zeolitic microcapsular reactor, the external surfaces of the foregoing Pd preloaded MSSs were seeded with 60 nm silicalite-1 nanocrystals [58] via a layer-by-layer procedure described previously [52–55] and then treated through a two-step hydrothermal approach. Briefly, 0.1 g of nanozeolite seeded sample was hydrothermally treated in 15 mL of 1.5 wt% TPAOH aqueous solution at 100 °C for 1.0 h, and then continuously treated in 15 mL aqueous solution with a molar composition of TPAOH:TEOS:H<sub>2</sub>O = 3:10:2000 at 100 °C for 8 h. The solid product was separated by centrifugation and washed with distilled water three times. All of the organic ingredients in the samples were removed by calcination in air at 550 °C for 6 h. Finally, a reduction process was adopted in a continuous hydrogen flow at 100 °C to obtain the metallic Pd-encapsulated Pd@S1 catalyst. The blank zeolite microcapsules without the Pd encapsulation were fabricated according as described previously [55] and were used as the reference sample.

### 2.3. Catalyst characterization

The SEM and TEM images of the catalysts were obtained on Philips XL30 and JEOL JEM-2010 instruments with accelerating voltages of 20 and 200 kV, respectively. The XRD patterns were obtained on a Rigaku D/MAX-IIA diffractometer over a  $2\theta$  range of 5°–70° with CuK $\alpha$  radiation. The UV–vis spectra were recorded on a Shimadzu UV-2450 UV–vis spectrophotometer. The XPS analysis was carried out with a Perkin-Elmer PHI 5000C ESCA system using AlK $\alpha$  radiation (1486.6 eV) at a power of 250 W. The pass energy was set at 93.9 eV, and the binding energies were calibrated by using contaminant carbon at a BE of 284.6 eV. All samples were heavily grinded to expose the Pd species before XPS measurement. The elemental analyses were performed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

### 2.4. Adsorption test of benzothiazole

The adsorption of benzothiazole was conducted to prove the protective effect of a zeolitic shell on Pd@S1. To do this, a 30-mg sample of Pd@S1 was added to 30 mL of benzothiazole solution with a concentration of  $3.0 \times 10^{-5}$  M in cyclohexane. For comparison, the blank zeolite microcapsule without Pd encapsulation and a shell-crushed Pd@S1 (prepared by heavily grinding the sample to expose the encapsulated Pd toward the

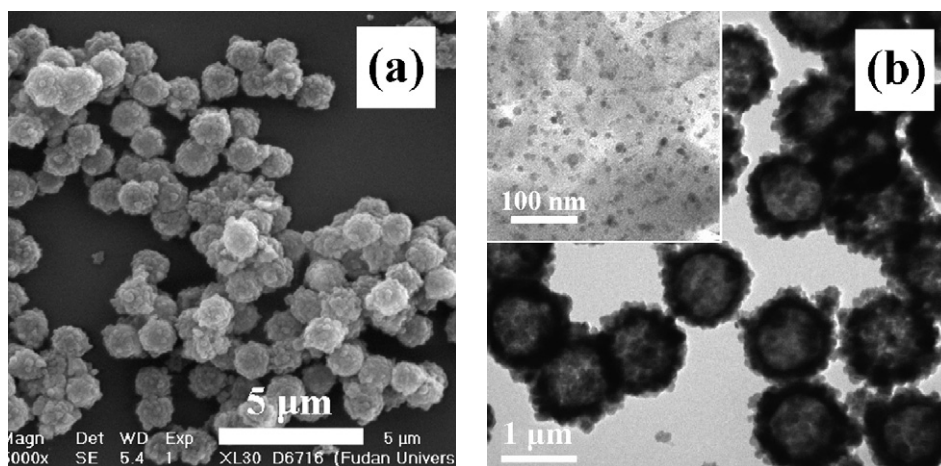


Fig. 1. SEM (a) and TEM (b) images of the prepared Pd@S1 catalysts. The inset in (b) is the TEM image at high magnification to depict the encapsulated Pd nanoparticles.

adsorbate) were tested under the same conditions. The variation of benzothiazole concentration was detected by UV–vis absorption at each time interval. The adsorption percentage was calculated by  $(C_0 - C_t)/C_0$ , where  $C_0$  and  $C_t$  refer to the concentration of the initial solution and that after adsorption for  $t$  min, respectively.

### 2.5. Typical procedure for the Heck reaction

Aryl halide (5 mmol), olefin (8 mmol),  $\text{Et}_3\text{N}$  (5 mmol, anhydrous), Pd catalyst (0.0125 or 0.025 mmol), and dodecane (1 mmol, as the internal standard) were sequentially introduced into a 50 mL flask fitted with a reflux condenser and a septum. Then the solvent (NMP, 30 mL) was added. The mixture was stirred at 120 °C for 3–8 h. After the reaction was completed, the used catalyst was recovered by filtration and washed with NMP for reuse, and the filtrate was collected and analyzed by FID-GC (using an HP5890-II gas chromatograph with a HP-5 capillary column), using dodecane as the internal standard, to determine the product yields.

The kinetic data were obtained by sampling a small quantity of the reaction mixture at 1, 1.5, 2, 2.5, and 3 h during the first, second, and tenth reaction runs. After centrifugation, the supernatant solution of the reaction mixture was collected and analyzed by FID-GC as described above.

## 3. Results

### 3.1. Catalyst characterization

Fig. 1 presents the typical SEM and TEM images of the Pd@S1 samples prepared through the hydrothermal transformation of nanozeolite-seeded, guest-preincorporated MSSs. The SEM images in Fig. 1a show the uniform spherical morphology of about 1–1.2  $\mu\text{m}$  and their dense shell composed of closely packed nanozeolite, whereas the TEM image in Fig. 1b clearly shows their hollow interior of about 1  $\mu\text{m}$  surrounded by a thin zeolitic shell of ca. 200 nm. The inset of Fig. 1b is a TEM image with high magnification, clearly showing the en-

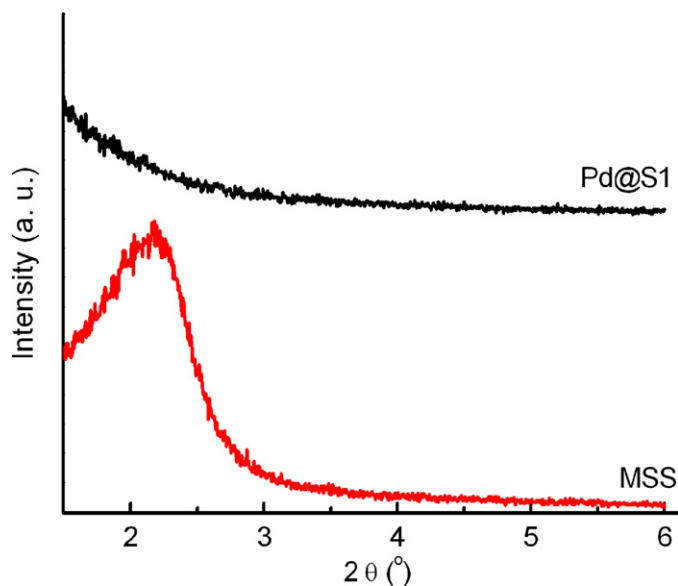


Fig. 2. XRD patterns of MSS template (red) and Pd@S1 (black) at low  $2\theta$  range. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

capsulated palladium nanoparticles (ca. 11 nm). The total Pd content in catalyst was measured as ca. 7.8 wt% by ICP-AES analysis.

The transformation of amorphous mesoporous MSS template into zeolitic shells can be proven by their XRD patterns in the low diffraction range (Fig. 2). As expected, the characteristic mesoscopic diffraction peak at ca. 2° of MSS disappeared, illustrating the complete consumption of its silica resource during the hydrothermal process. Fig. 3a shows the XRD pattern of the Pd@S1 catalyst in the wide diffraction range, in which the composition of the obtained material can be further verified. The sets of the diffraction peaks attributed to metallic palladium and silicalite-1 are both clearly shown.

Furthermore, the average size of the Pd nanoparticles in the catalyst was also calculated from the width of Pd(111) peak using Scherrer's formula. The average size of the Pd particles

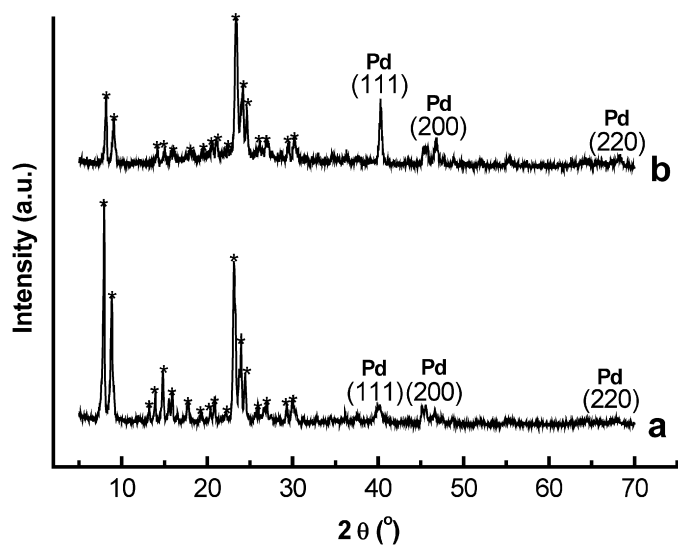


Fig. 3. XRD patterns of the fresh Pd@S1 catalyst (a) and that after ten runs of Heck coupling reaction (b). The characteristic peaks attributed to zeolite (silicalite-1) are indicated by \*.

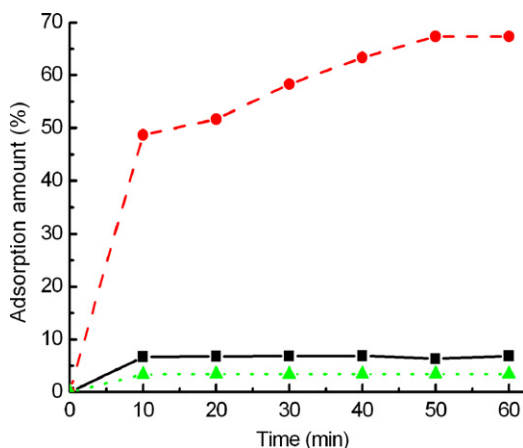


Fig. 4. The adsorption plot of benzothiazole on Pd@S1 (black, —), shell-crushed Pd@S1 (red, ---) and zeolite microcapsules without Pd encapsulation (green, ···). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

in Pd@S1 is 10.4 nm, which is in accordance with the TEM observations.

The encapsulation of palladium in the micrometer-sized hollow core of Pd@S1 and the intactness of the zeolitic shell can be proven by a benzothiazole adsorption experiment. Because of its large molecular size (preventing diffusion through the zeolitic shell) and selective interaction with Pd (via its nitrogen or sulfur atoms), benzothiazole is a good probe for detecting the Pd nanoparticles possibly left out of the zeolitic shell. To clearly determine the protective effect of the zeolitic shell, a “shell-crushed Pd@S1” sample with exposed Pd nanoparticles (see Section 2) was also tested under the same conditions. It was found that nearly 70% of the benzothiazole in the solution was adsorbed by the “shell-crushed” sample in 1 h (Fig. 4, red dash line), with <3% adsorption on Pd@S1 with an intact silicalite-1 shell even after deducting that on the blank zeolitic microcap-

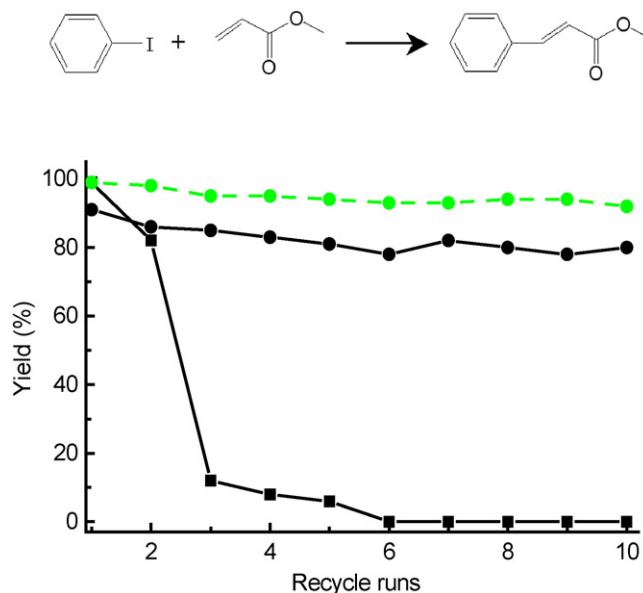


Fig. 5. The Heck coupling activity and reusability of Pd@S1 (●) and Pd/C (■). Reaction conditions: 5 mmol of aryl halide, 8 mmol of olefin, 5 mmol of anhydrous triethylamine (Et<sub>3</sub>N), 0.0125 mmol of Pd and 30 mL of NMP under stirring at 120 °C for 3 h. The green dashed plot was obtained by doubling the amount of Pd@S1 catalyst (i.e., 0.025 mmol Pd), which shows that a higher yield of nearly 100% could be reached with higher catalyst amount. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

sule without incorporation of Pd (Fig. 4). This finding indicates that the most of the Pd nanoparticles in our Pd@S1 samples were effectively entrapped inside the intact zeolitic shell.

### 3.2. Catalytic test

The Heck coupling reaction of iodobenzene with methyl acrylate was chosen as the model reaction for testing the efficiency of our Pd@S1 catalyst. The reaction was carried out in 30 mL of NMP at 120 °C using triethylamine as a base. The amounts of iodobenzene and methyl acrylate were 5 and 8 mmol, respectively, and the catalyst amount corresponded to 0.0125 mmol of Pd (i.e., Pd/PhI = 0.0025). For comparison, an industrial Pd/C catalyst was tested under the same reaction conditions. The results, shown in Fig. 5, clearly demonstrate that both catalysts were effective in the first run of reaction. The reaction was completed in 3 h and achieved a high yield (>90%) of *trans*-methyl cinnamate.

Compared with conventional Pd/C catalyst, Pd@S1 demonstrates superior reusability and stability. The Pd/C deactivates quickly in two or three cycles, whereas the Pd@S1 can retain its high yields of the target product even after up to 10 recyclings (Fig. 5). This property obviously can be attributed to the protective effect of the zeolitic shell. Furthermore, according to the TEM images shown in Fig. 6, the used Pd@S1 particles can retain their dense zeolitic shell even after 10 recyclings, indicating a promising stability of Pd@S1 in liquid reaction.

To further prove the antileaching effect of the zeolitic shell, the leaching percentage of the Pd from the catalysts were derived from the ICP-AES analysis of Pd concentration in the



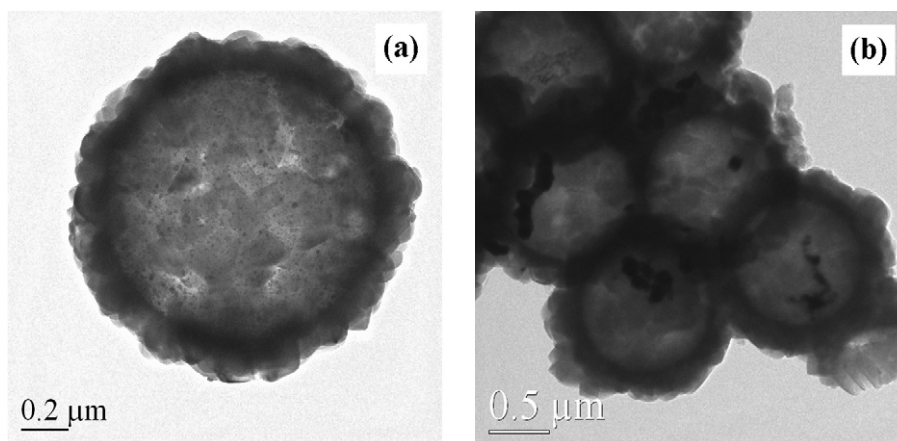
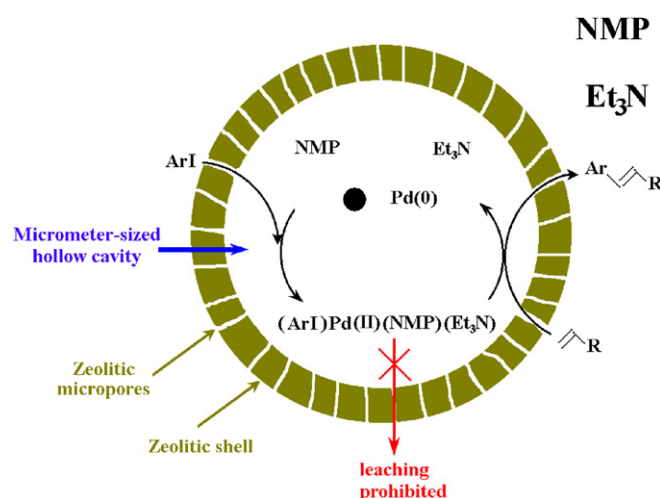


Fig. 6. TEM images of fresh Pd@S1 catalyst (a) and that after ten cycles of Heck coupling reaction (b).

reaction solutions after the catalysts were filtered off. It was found that about 30% of the Pd in fresh Pd/C was leached out after the first catalytic reaction, compared with only 2% in Pd@S1 catalyst (probably due to the small amount of exposed Pd in a few broken microcapsules). The leaching in Pd@S1 was negligible in the subsequent reaction cycles, considering the detection limit of the ICP-AES instrument. The low Pd leaching in Pd@S1 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, especially in pharmaceutical production.

Table 1 characterizes the applicability of Pd@S1 reactor in Heck coupling reactions of various aryl iodides and olefins. It is shown that all three aryl iodides can be coupled with methyl acrylate or styrene to provide the respective product. Even 4-iodotoluene bearing a deactivating electron-donating group in the *para*-position of the phenyl ring can be used. The electron-rich heterocycle 2-iodothiophene works equally well (Table 1, entries 6 and 7), indicating that this nanopalladium-microcapsulated catalyst displays as high a catalytic efficiency as their homogeneous analogues. When methyl acrylate was chosen as the olefin, the high yield (>90%) could be obtained in relatively shorter periods (e.g., 3 h) (Table 1, entries 1, 3, 6). However, when styrene is used as the substrate, prolonging the reaction time and increasing the catalyst amount seem to be necessary to achieve a yield of 70–80% (Table 1, entries 2, 4, and 7). This can be attributed either to the relatively low reactivity of styrene [3,59] or to the possible diffusion resistance of the relative large reactants/products in the zeolitic shell. Moreover, when an aryl halide with the diameter larger than the pore size in silicalite-1 shell (e.g., 5-iodo-*m*-xylene) is used as the reactant (Table 1, entry 5), our catalysts have a very low product yield (4.2%), because of the shape-selectivity of the zeolitic shell. However, after the zeolitic shell in our catalyst was destroyed by heavy grinding, the shell-crushed Pd@S1 displayed a very high product yield of 92%, close to that of Pd/C with exposed Pd species (97%). These results further demonstrate the completeness of the zeolitic shell in our Pd@S1 catalyst.

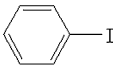
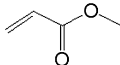
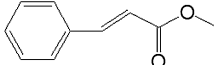
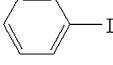
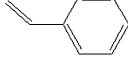
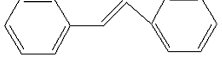
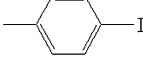
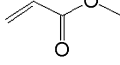
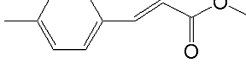
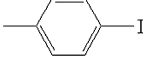
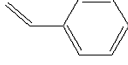
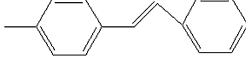
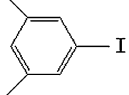
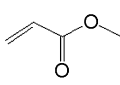
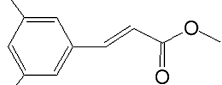
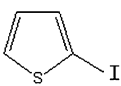
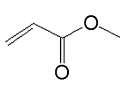
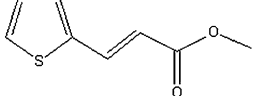
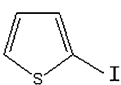
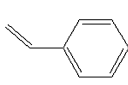
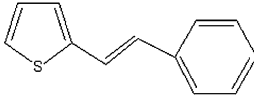


Scheme 1. Schematic illustration for the engaged quasi-homogeneous Heck-coupling in Pd@S1 catalyst.

#### 4. Discussion

The most interesting features of Pd@S1 that can be derived from the foregoing results are its promising stability and reusability due to the encapsulation of active Pd species inside the zeolitic shell. It has been reported that the metallic Pd-catalyzed Heck coupling reaction is essentially a quasi-homogeneous catalytic process occurring via either a palladium complex intermediate [7] or solvated palladium clusters [6,9] in the system of aryl iodides and aprotic polar solvents. Heck coupling on the Pd@S1 catalyst may follow a similar mechanism but within the micrometer-sized hollow cavities, as illustrated in Scheme 1. Adding the aryl halide to the reaction solution triggers an oxidative addition to palladium atoms in the Pd nanoparticles with the aid of NMP and Et<sub>3</sub>N, thus forming a soluble active Pd(II) complex intermediate [7]. Then the active intermediate reacts with olefin to complete the catalytic cycle. Once all of the aryl halides are consumed, the palladium complex finally returns to its metallic state and re-deposits onto the surface of the support. Notably, unlike that in the classical supported palladium catalyst, the formed active [Pd(II)(ArI)(NMP)(Et<sub>3</sub>N)] intermediate in our catalyst is

Table 1  
Heck coupling for various substrates<sup>a</sup>

Entry	Aryl halide	Olefin	Time (h)	Product	Yield (%) <sup>b</sup>
1			3		93 (99 <sup>c</sup> )
2			7		70 (80 <sup>c</sup> )
3			4		94
4			8		57 (75 <sup>c</sup> )
5			4		4.2 (92 <sup>d</sup> )
6			3		97
7			7		70

<sup>a</sup> Reaction conditions: aryl halide (5 mmol), olefin (8 mmol), anhydrous triethylamine (5 mmol), Pd (0.0125 mmol) and 30 mL of NMP under atmosphere, 120 °C.

<sup>b</sup> Yields were determined by GC analysis using dodecane as the internal standard and were obtained by the ratio of the product amount/theoretical value supposing the complete consumption of the aryl halides.

<sup>c</sup> Yields obtained by doubling the Pd@S1 amount.

<sup>d</sup> Yield obtained on shell-crushed Pd@S1 under the same condition.

engaged in the micrometer-sized hollow cavities of the zeolitic microcapsular reactor, because its molecular diameter is relatively larger than the pore size in the zeolitic shell (silicalite-1). With this protective effect of the surrounding zeolitic shell, a stable catalyst for Heck coupling could be constructed by engaging the quasi-homogeneous process into a unique microenvironment in the hollow interior of Pd@S1.

To prove the existence of the engaged quasi-homogeneous mechanism in Pd@S1, we conducted a two-step test originally proposed by Biffis et al. [6]. All of the reaction conditions were the same as those for the Heck coupling test, except omitting the addition of olefins in the first step [60]. After 5 h, the catalyst was filtered off and the second step in the reaction was continued by adding methyl acrylate to the filtrate. As expected, only trace amounts of the product could be detected even after the filtrate was reacted for another 5 h, indicating an absence of the leached palladium species in the solution.

In another approach, an XPS experiment was carried out on the filtered catalyst after the first step of the reaction (Fig. 7). In contrast to the fresh catalyst, in which Pd is mainly 0 valent (centered at 335 eV for Pd 3d<sub>5/2</sub>, in Fig. 7), the Pd in the filtered catalyst is mainly +2 valent (centered at 336 eV for Pd 3d<sub>5/2</sub>), indicating that a palladium(II) complex indeed forms in the interior of the Pd@S1 during the reaction. The dissolving-redepositing process of the encapsulated palladium nanoparticles also can be verified by the Ostwald ripening of some Pd nanoparticles after reaction [7]. As shown in Figs. 3b and 6b, the 10-times-recycled Pd@S1 catalyst exhibits sharp-

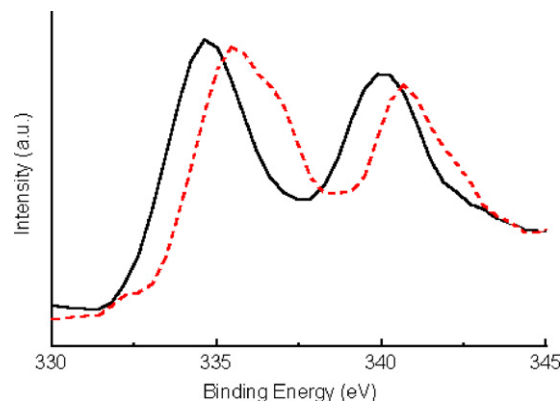


Fig. 7. XPS Pd 3d spectra of fresh Pd@S1 (black, —) and filtered Pd@S1 after the first step reaction on Biffis test (red, ---). All the samples were washed with acetone, dried and heavily grinded to expose the Pd species before XPS characterization. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ened Pd diffraction peaks and obvious growth of Pd nanoparticles. The effect of the activity derived from the growth of the encapsulated Pd particles is indicated by the kinetic behavior of the Pd@S1 catalyst in the first, second, and tenth reaction runs (Fig. 8). It can be clearly seen that the steady activity of the catalyst changes little even after the tenth run (also see Fig. 5), and that the kinetic curves of the second and tenth runs exhibit the same trend, demonstrating that growth of such Pd species has a slight affect on activity, probably due to the quasi-homogeneous

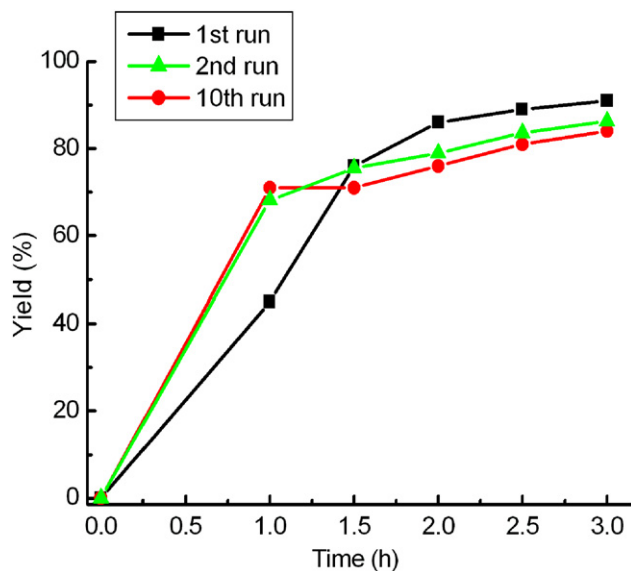


Fig. 8. Kinetic results of Pd@S1 catalyst in the 1st, 2nd and 10th runs.

mechanism. A similar phenomenon has been reported in the literature [7]. Moreover, a relatively low increase in activity is evident in the initial reaction period during the first run, possibly attributed to the induction process of Pd species [33,50] for the fresh catalyst.

The engaged Heck coupling reaction in our catalyst can be further proved by the different behaviors of *para*- and *ortho*-substituted aryl halides (Table 1). When the catalysts with the exposed Pd species, such as shell-crushed Pd@S1 and Pd/C, are applied, both 4-iodo-toluene and 5-iodo-*m*-xylene demonstrate high reactivity (yield >90%). However, for our Pd@S1, which has a protective zeolitic shell, only the *para*-substitute reactant with relative small size can permeate into the zeolitic shell and be successfully converted on the encapsulated Pd species (yield 94%; Table 1). The reactivity of the *ortho*-substituted reactant is negligible (yield only 4.2%; Table 1) because of its larger-than-micropore size in the zeolitic shell. Considering that both reactants should follow the same mechanism, the Heck coupling reaction in our catalyst must proceed in the interior of our catalyst via an engaged quasi-homogeneous mechanism.

## 5. Conclusion

A new strategy of encaging quasi-homogeneous catalysis into the zeolitic microcapsules is proposed for the design of reusable, highly efficient catalysts. To prove the feasibility of such ideal, a novel nanopalladium-entrapped zeolitic microcapsular reactor was successfully fabricated for catalyzing a series of Heck coupling reactions. As expected, our Pd@S1 catalyst demonstrates high activity even under a relatively low Pd adopted amount (Pd/PhI = 0.0025). More importantly, due to the antileaching effect of the surrounding zeolitic shell toward the entrapped homogeneous Pd species, Pd@S1 shows outstanding stability and reusability even in the leaching-prone reaction system containing aprotic polar solvent (NMP) and aryl iodides.

As a general conclusion, we should point out that the heterogenization of the homogeneous catalyst is an eternal theme due to the combination of the efficiency of the homogeneous catalyst and the durability of the heterogeneous catalyst. The approach of encapsulating a homogeneous catalytic microenvironment in a porous inorganic shell could provide a novel and beneficial route for the rational design of catalysts in this domain, which may find new opportunity to achieve complex industrial and fine-chemical synthesis through sequentially integrating the diverse active blocks.

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