Journal of Molecular Catalysis A: Chemical 323 (2010) 16–22

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

A new method for the preparation of microcapsule-supported palladium catalyst for Suzuki coupling reaction

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ARTICLE INFO

Article history:
Received 25 November 2009
Received in revised form 1 February 2010
Accepted 23 February 2010
Available online 3 March 2010

Keywords:
Microcapsule-supported palladium catalyst
Phosphine ligand
Suzuki coupling reaction
Recycle

ABSTRACT

In this paper, a new method for the preparation of microcapsule-supported palladium catalyst for Suzuki coupling reaction was described. The highly monodispersed cross-linked polystyrene microcapsules containing phosphine ligand were synthesized by the self-assembling of phase separated polymer (SaPSeP) method using diphenyl(4-vinylphenyl)phosphine and divinylbenzene as a monomer and cross-linking agent, respectively, and 2,2′-azobisisobutyronitrile (AIBN) as an initiator within the droplets of oil-in-water (O/W) emulsions, which were prepared by using the Shirasu porous glass (SPG) membrane emulsification technique. The microcapsule-supported palladium catalyst was obtained by treating the microcapsules with a solution of $Pd_2(dba)_3$ in dichloromethane. This supported palladium catalyst exhibited high catalytic activity for the Suzuki coupling reaction of various aryl bromides and can be reused several times without the loss of activity.

1. Introduction

In catalytic organic synthesis, polymer-supported transition metal catalysts offer the following advantages over the usual homogeneous catalysts: easy recovery and potential recycling of expensive catalysts, simplified product purification and the possibility of carrying out the desired transformation in a continuous-flow system. Therefore, polymer-supported catalysts, which are often considered as heterogenized homogeneous catalysts, have attracted considerable attention over the past years [1–5]. The methods for the preparation of polymer-supported catalysts can broadly be separated into two groups: in the first, a polymer is prepared by first using a monomer bearing ligand moiety, before the catalyst is anchored to the polymer through a complexation reaction between the transition metal atom and ligand moiety on the polymer. In the second, a polymer is modified by a ligand, and then the catalyst is attached to the polymer through the method mentioned above. Transition metal complexes of polymer-supported catalysts are usually linked to the polymer chain, and protrude into the reaction solvent. This leads to the loss of catalyst activity when they are recovered by filtration and recycled due to the leaching of active catalyst species from polymeric support.

To resolve the above mentioned problem, Ley [6] and Kobayashi [7] have carried out independent ground-breaking work using microencapsulation techniques. However it was demonstrated, by way of a three-phase test, that commercially available PdEnCat catalysts act as heterogeneous sources, or reservoirs, for soluble, catalytically active species [8]. This behavior of PdEnCat catalysts may lead to the leaching of active catalyst species. By the microencapsulation and cross-linking of polymer chains, Kobayashi and co-workers used phosphinated polymers to prepare polymer incarcerated (PI) palladium catalysts. In the cross-linking process, some phosphines were oxidized to the corresponding phosphine oxides, and $HSiCl_3$ reduction was needed to produce phosphinated PI Pd [9]. In addition, the size of microcapsules and the existing mode (inside or outside) of phosphine ligands could not be controlled when this method was employed.

Here we wish to report a new method for the preparation of a microcapsule-supported palladium catalyst for the Suzuki coupling reaction. The principle of the preparation is schematically described in Scheme 1. At first, monodispersed size-controllable microcapsules containing phosphine ligands were prepared by the Shirasu porous glass (SPG) emulsification technique [10] using diphenyl(4-vinylphenyl)phosphine and divinylbenzene as a monomer and cross-linking agent, respectively. Palladium was then attached to the interior of the microcapsules. These newly formed microcapsules acted as microreactors in which the catalysis occurred. Even if palladium species dissociate from one phosphine ligand, it may attach to another phosphine ligand inside of the microcapsule. Therefore, the microcapsule-supported palladium catalyst is very

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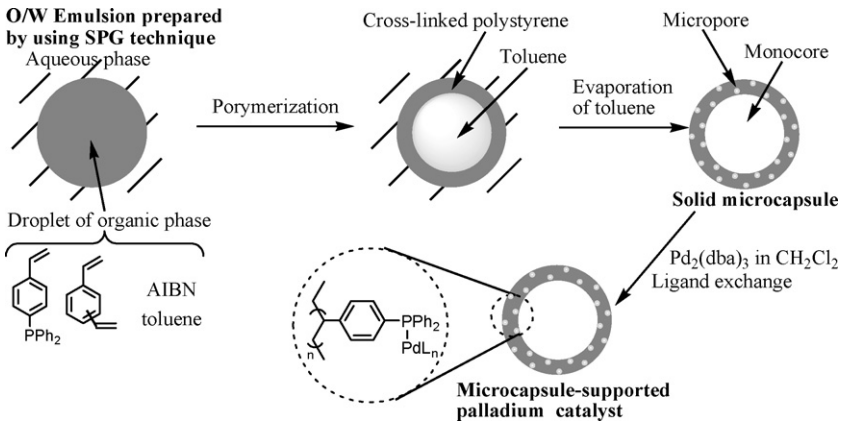
doi:10.1016/j.molcata.2010.02.029



Scheme 1. Schematic illustration for the preparation of the microcapsule-supported palladium catalyst.

stable, and can be reused several times without loss of activity.

2. Experimental

2.1. Reagents and materials

Polyvinyl alcohol (PVA, Mn ≈ 1170) and sodium dodecylsulfate (SDS) were used as received. Divinylbenzene (DVB) was washed with 10% sodium hydroxide and water, dried with $CaCl_2$, and then distilled from calcium hydride before being used. 2,2′-Azobisisobutyronitrile (AIBN) was recrystallized from ethanol. Bromobenzene (ABCR, 99%), 2-bromotoluene (Acros, 99%), 4-bromoacetophenone (Alfa Aesar, 98%), 4-bromoanisole (ABCR, 99%), 4-bromophenol (Acros, 97%), 1-bromo-2,4,5-trifluorobenzene (ABCR, 99%), 1-bromo-4-nitrobenzene (Aldrich, 99%), 4-bromo-*N*,*N*-dimethylaniline (Aldrich, 97%), 4-fluorobromobenzene (ABCR, 98%), 3-bromopyridine (Acros, 99%), 4-bromobenzaldehyde (Alfa Aesar, 99%), 2-bromobenzaldehyde (Alfa Aesar, 98%), 4-bromo-2-fluorobenzaldehyde (Acros, 97%), 1-bromonaphthalene (ABCR, 98%), $Pd_2(dba)_3$, phenylboronic acid and K_2CO_3 were used in their commercially available form. Shirasu porous glass (SPG) membrane was obtained from the Fujikin incorporation of Japan. Double-distilled deionizing water was used in the present experiments. Other analytical reagents were used as received.

2.2. Preparation of monodispersed hollow microcapsules

The emulsification procedure was carried out by utilizing a hydrophilic SPG membrane emulsification kit with average pore size of 2.8 μm. Prior to emulsification, the membrane was soaked in deionized water containing a small amount of SDS for over 30 min after ultrasonic treatments. Then, the SPG membrane was installed into the SPG membranes module as a filter media. The dispersed phase consisting of 4-styryldiphenylphosphine (SDPP, 10 mmol, 2.88 g), DVB (2.5 mmol, 0.72 g), AIBN (3 wt% of monomers) and toluene (2.4 mL) was poured into a pressure tight vessel, and allowed to permeate into the continuous phase containing PVA (1.0 wt%), SDS (0.3 wt%) and deionized water (60 mL) through the hydrophilic membrane under nitrogen gas pressure.

The obtained emulsion was transferred into a three-neck bottle glass that had a condenser, a magnetic stirrer and a nitrogen inlet nozzle. Emulsion polymerization was carried out for 24 h at 70 °C under nitrogen atmosphere. After the polymerization had finished, the reaction mixture was cooled to room temperature and methanol was added for the precipitation of the polymer particles. The polymer particles were then washed with deionized water, methanol, acetone, dichloromethane and methanol successively, and dried in vacuum. The white powder of the microcapsule particles was obtained in 52% yield (1.87 g).

2.3. Preparation of microcapsule-supported palladium catalyst

A solution of $Pd_2(dba)_3$ in CH_2Cl_2 was added to the microcapsules (1.0 g) swelled in the dry CH_2Cl_2 (10 mL). The mixture obtained was then stirred at room temperature under N_2 atmosphere for 3 h. This microcapsule-supported palladium catalyst was obtained by ligand-exchange reaction. The content of Pd in the microcapsules was determined by inductively coupled plasma (ICP) after the microcapsules were filtrated and washed with CH_2Cl_2 (10 mL ×2) as well as dried in a vacuum.

2.4. General procedure for Suzuki coupling reaction

Aryl bromides (0.5 mmol), phenylboronic acid (1.5 equiv.), K_2CO_3 (1.5 equiv.), microcapsule-supported Pd(0) catalyst containing 1 mol% Pd catalyst, and IPA (2 mL) were added to a Schlenk reactor. The mixture was put in a preheated oil bath at a given temperature of 80 °C and stirred for 2–5 h. After completion of the reaction, the mixture was cooled to room temperature, and the catalyst was collected by filtration, washed with acetone, water and ethanol, then dried under vacuum and reused. The organic filtrate was evaporated under vacuum to give a crude product. The crude product was further purified by flash chromatography using silica gel (EtOAc/Petroleum) to give the desired coupling product.

2.5. Three-phase test

Silica gel supported aryl bromide was prepared according to the literature procedure [11]: a solution of 3-aminopropyl triethoxysilane (5.1 mL, 22.0 mmol) in dry THF (10 mL) was added dropwise to a solution of 4-bromobenzoyl chloride (4.83 g, 22.0 mmol) and triethyl amine (3.2 mL, 22.0 mmol) in dry THF (50 mL) at −15 °C under nitrogen atmosphere. The resulting mixture was warmed to room temperature, and stirred for 2 h. Then the solid was removed via filtration and the solvent was removed under vacuum at room temperature, giving 8.5 g of the desired product, 4-bromobenzamide 3-propyltriethoxysilane as a beige solid.

A mixture of 4-bromobenzamide 3-propyltriethoxysilane (8.5 g, 21.9 mmol) thus obtained and pyridine (2.3 mL, 29.4 mmol) was added dropwise to a suspension of silica (2.0 g) in dry toluene (50 mL) under nitrogen atmosphere. The resulting mixture was refluxed for 24 h. And then the suspension was filtered and Soxhlet extracted with dichloromethane for 24 h. The resulting solid was dried under vacuum at room temperature, giving 2.4 g of white

powder, and the content of aryl bromide was 1.64 mmol/g determined by elemental analysis.

A solution of 4-bromobenzamide (0.25 mmol), phenylboronic acid (0.38 mmol, 1.5 equiv.), and K_2CO_3 (0.38 mmol, 1.5 equiv.) in IPA (2 mL) was stirred in the presence of microcapsule-supported Pd catalyst (1.0 mol% Pd) and silica gel supported aryl bromide (192 mg) at 80 °C for 4 h. And then the supernatant was analyzed by GC and the solid was separated by filtration, washed with ethanol, and further extracted with dichloromethane. The solid was then hydrolyzed with 2 M KOH in ethanol/water (1.68 g, 10 mL of EtOH, 5 mL of H_2O) at 90 °C for 3 days. The resulting solution was neutralized with aqueous HCl (10 wt%), extracted with dichloromethane followed by ethyl acetate, concentrated, and the resulting mixture was analyzed by ^{1}H NMR.

2.6. General characterization

Photographs of microcapsules were taken by a TE2000-S (Nikon Eclipse) optical microscope. The scanning electron microscope (SEM) measurements were conducted by using a JSM-6700 III (JEOL Co., Tokyo, Japan) electron microscopy. The ratio of phosphorus to carbon on the surface of microcapsules was determined by SEM with an EDX (JEM-6700, Oxford INCA) attachment. The transmission electron microscope (TEM) measurements were conducted using a Tecnai G22oS-Twin electron microscopy at an acceleration voltage of 200 kV. A small drop of a suspension of microcapsules in ethanol was deposited onto a carbon-coated copper grid and dried at room temperature. The ratio of phosphorus to carbon in the whole microcapsule was determined by TEM with an EDX (Noran Instru.) attachment. The diameter distribution of the microcapsule particles was determined by a LSTM 100Q laser diffraction particle size analyzer. The amount of Pd was obtained by inductively coupled plasma (ICP) atomic emission spectrometry (Optima 2000 DV). The thermal stability of the microcapsules was studied by thermal gravimetric analysis (TGA) using a TGA/SDTA851e (Mettler-Toledo Co., Sweden) TGA instrument in temperatures ranging from 0 to 600 °C with a heating rate of 10 °C/min. The ^{1}H NMR spectra were recorded on a Bruker Avance II 400 MHz spectrometer using $CDCl_3$ as the solvent.

3. Results and discussion

3.1. Synthesis and characterization of the microcapsule-supported palladium catalyst

The highly monodispersed cross-linked polystyrene microcapsules containing phosphine ligand were synthesized by the self-assembling of phase separated polymer (SaPSeP) method [12,13] using diphenyl(4-vinylphenyl)phosphine and divinylbenzene as a monomer and cross-linking agent, respectively, and AIBN as an initiator within the droplets of oil-in-water (O/W) emulsions, which were prepared by using the SPG membrane emulsification technique.

During the preparation of microcapsules, we found that in this method of microcapsule preparation, the solvent plays an important role in getting the phosphine ligand inside the microcapsule. Therefore, the influence of solvent in the organic phase was investigated by using different solvents such as dichloromethane, hexadecane, dodecanol, and toluene. Among the solvents investigated, toluene gave the lowest ratio of phosphorus to carbon on the surface of the microcapsule (0.89%) determined by energy-dispersive X-ray (EDX) spectrometry combined with scanning electron microscope (Fig. 1, upper) [14], which indicated that 90% of phosphine ligands existed inside the microcapsule (ratio of phosphorus to carbon on the whole microcapsule was 8.90% determined

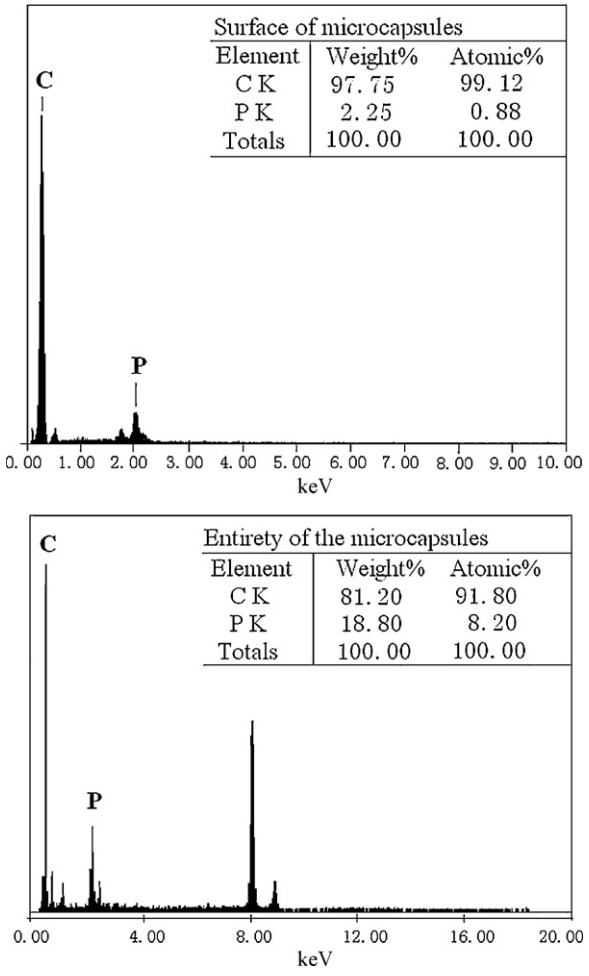


Fig. 1. Energy-dispersive X-ray (EDX) analysis spectra of the surface of the microcapsules (upper), and the entirety of the microcapsules (lower).

by EDX combined with transmission electron microscope, Fig. 1, lower) [15]. The optical micrograph (OM, after swelled for 7 h in toluene), scanning electron microscope (SEM) images and diameter distribution of the microcapsule particles are shown in Figs. 2–4. As shown in Figs. 2 and 3, the size of the prepared microcapsules was uniform. The average diameter and the coefficient of variation (CV) of the microcapsule particles are 7.78 μm and 15.42%, respectively. Fig. 5 shows the transmission electron microscope (TEM) images of the microcapsules after drying under vacuum,

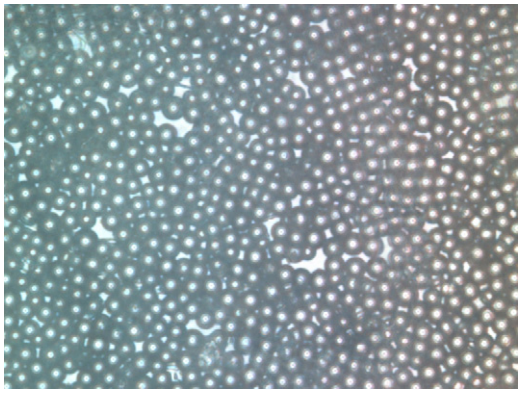


Fig. 2. Optical micrograph (400× magnification) of microcapsules containing phosphine ligand.

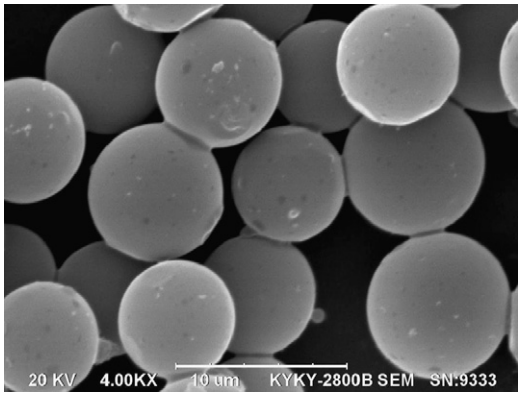


Fig. 3. SEM image of microcapsules containing phosphine ligand.

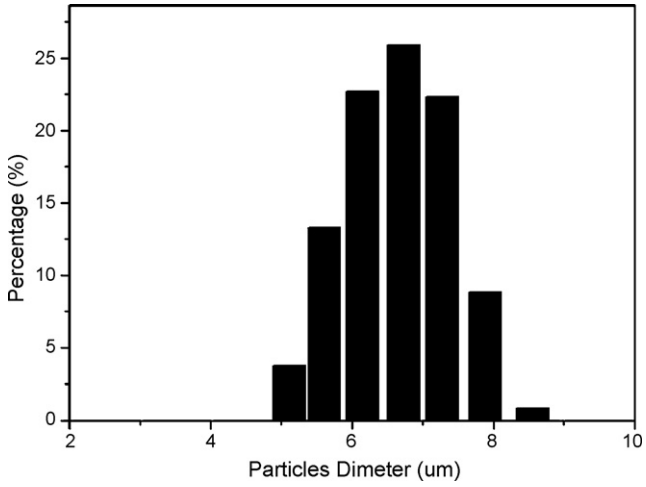


Fig. 4. Diameter distribution of microcapsules containing phosphine ligand.

which clearly indicate that the microcapsules prepared possess a hollow structure. The thermal stability of the microcapsules was also studied by thermal gravimetric analysis (TGA) in temperatures ranging from 0 to 600 °C with a heating rate of 10 °C/min (Fig. 6). The weight loss occurred from the temperature of around 200 °C that means the microcapsules are stable under the temperature of 200 °C. The microcapsules were then treated with $Pd_2(dba)_3$

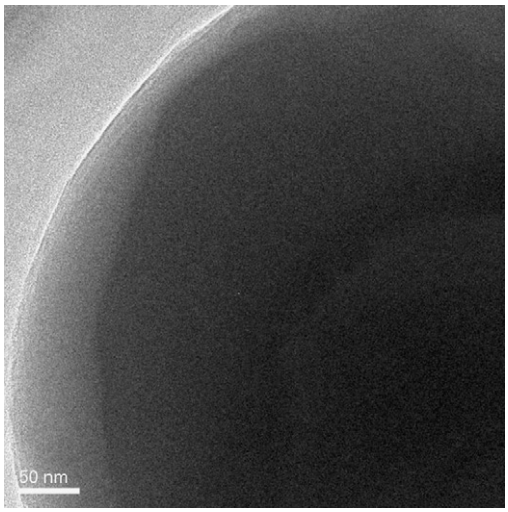


Fig. 5. TEM images of the microcapsules after drying under vacuum.

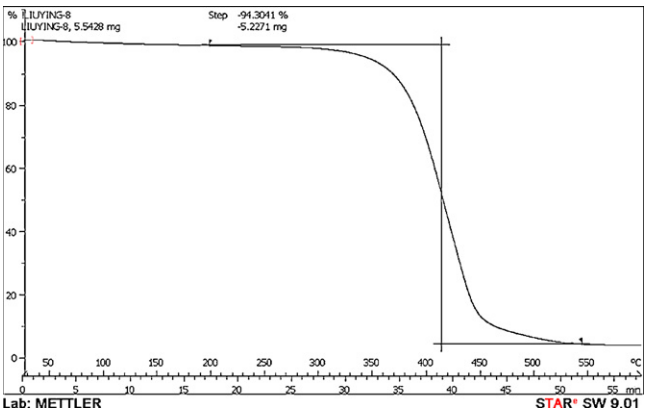
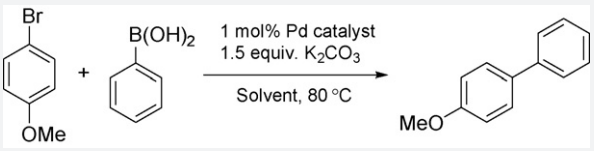


Fig. 6. The weight loss curve of the microcapsules determined by TGA.

Table 1
Solvent effect on the Suzuki coupling reaction of 4-bromoanisole with phenylboronic acid catalyzed by microcapsule-supported palladium[a].



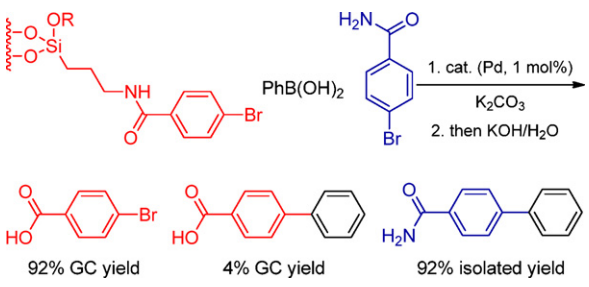
Entry	Solvent	Time (h)	Yield (%)[b]
1	Toluene	2	64
2	Toluene/IPA(1/1)	2	91
3	IPA	2	99
4	Ethanol	4	63
5	1,2-Dioxane	4	32
6	DME	4	51
7	DMF	2	96

[a] *Reaction conditions:* 4-bromoanisole (0.5 mmol), phenylboronic acid (1.5 equiv.), K_2CO_3 (1.5 equiv.), 1 mol% Pd catalyst (12.5 mg), IPA (2 mL), 80 °C.
[b] Isolated yield.

in dichloromethane to obtain the microcapsule-supported palladium catalyst by ligand-exchange reaction. Inductively coupled plasma (ICP) analysis indicated that the ratio of Pd was 2.17 wt%, and the EDX determination shows that no Pd existed on the surface of microcapsule, which clearly indicated the Pd was completely immobilized inside the microcapsule.

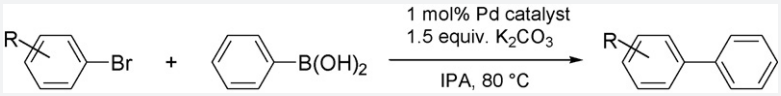
3.2. Suzuki coupling reaction catalyzed by microcapsule-supported palladium catalyst

The Suzuki-type cross-coupling reaction between aryl bromides and phenylboronic acid was chosen to evaluate the catalytic activity and stability of the microcapsule-supported palladium catalyst [16,17]. As is known, the solvent has a strong influence on the C–C bond forming reaction catalyzed by polymer-supported tran-



Scheme 2. Three-phase test in the Suzuki reaction with microcapsule-supported Pd.

Table 2
Suzuki coupling reaction of aryl bromides with phenylboronic acid catalyzed by microcapsule-supported palladium[a].



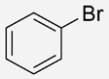
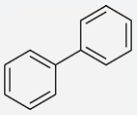
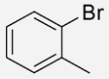
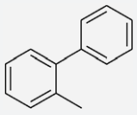
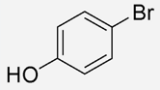
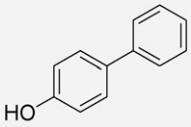
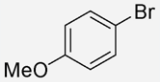
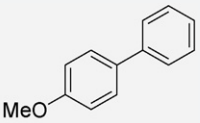
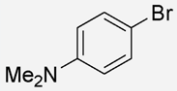
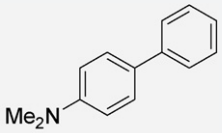
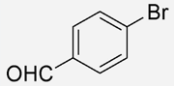
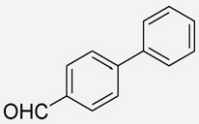
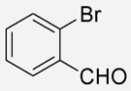
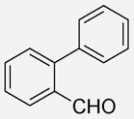
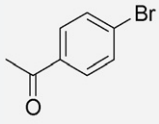
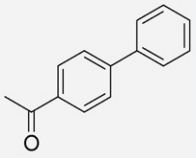
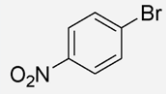
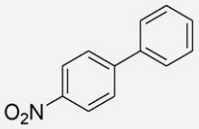
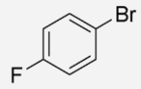
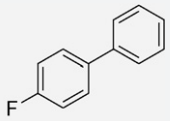
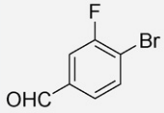
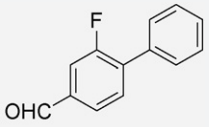
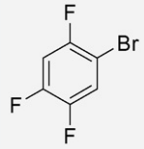
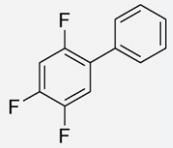
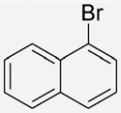
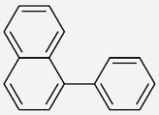
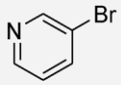
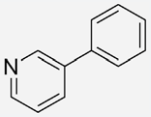
Entry	Aryl bromide	Time (h)	Product	Yield (%)[b]
1		2		92
2		3		67
3		3		81
4		2		99
5		3		88
6		3		85
7		5		15
8		2		97
9		3		98
10		3		82
11		3		58
12		2		71

Table 2(*Continued*).

Entry	Aryl bromide	Time (h)	Product	Yield (%)[b]
13		3		88
14		5		87

[a] *Reaction conditions:* aryl bromide (0.5 mmol), phenylboronic acid (1.5 equiv.), K_2CO_3 (1.5 equiv.), 1 mol% Pd catalyst (12.5 mg), IPA (2 mL), 80 °C. The reaction progress was monitored by TLC.
[b] Isolated yield.

sition metal catalysts [18,19]. The solvent was initially screened for the model reaction of 4-bromoanisole with phenylboronic acid, the results of which are shown in Table 1. Because polystyrene swells easily in toluene, the toluene was first utilized as a solvent, and 64% isolated yield of 4-methoxybiphenyl was obtained (entry 1). To enhance the solubility of base, K_2CO_3, a mixture of toluene and isopropanol (IPA) was subsequently examined, an excellent yield was obtained (91%, entry 2). Pleasingly, when the IPA was used as a solvent in the absence of toluene, an excellent yield was also obtained (99%, entry 3). The solvents, ethanol, 1,2-dioxane and 1,2-dimethoxyethane (DME), gave low yields (63%, 32% and 51%, respectively; entries 4–6) despite the reaction time being prolonged to 4 h. As expected, an excellent yield was also obtained when the *N*,*N*-dimethylformamide (DMF) was used as a solvent (96%, entry 7). Because IPA is readily available and inexpensive with low toxicity [20,21], it was employed as a solvent in the subsequent study.

Suzuki reactions of a wide range of aryl bromides with phenylboronic acid were tested, the catalysis results of which are summarized in Table 2. The reaction of bromobenzene with phenylboronic acid proceeded smoothly to offer biphenyl in 92% yield (entry 1). However, the 2-methyl phenyl bromide gave only moderate reaction yield (67%, entry 2), due to the steric hindrance of ortho-methyl group. The properties of substitutes at the para position of the aromatic ring did not have any influence on the reaction yields. The coupling reactions of phenyl bromides bearing electron-donating groups or electron-withdrawing groups on para position with phenylboronic acid were completed within 2–3 h and gave good to excellent yields (81–99%, entries 3–6, 8–10). Only 15% yield of 2-phenylbenzaldehyde was obtained when the 2-bromobenzaldehyde was treated with phenylboronic acid (entry 7). Fluorinated substrates, 4-bromo-3-fluorobenzaldehyde and 1-bromo-2,4,5-trifluorobenzene, were also examined, and moderate reaction yields were obtained (58% and 71%, respectively, entries 11 and 12). A good yield was obtained from the reaction of 1-bromonaphthalene with phenylboronic acid (88%, entry 13). Finally, 3-bromopyridine, a brominated aromatic heterocycle, was tested, and the desired coupling product was obtained in 87% yield (entry 14).

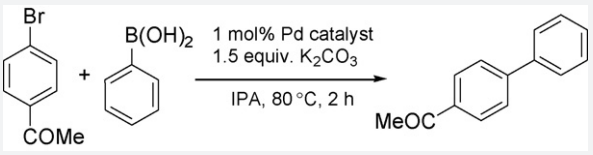
3.3. Recycled use of the microcapsule-supported palladium catalyst

The stability of microcapsule-supported palladium catalyst was then investigated, the results of the repeated use of the catalyst for the coupling reaction of 4-bromoacetophenone with phenylboronic acid are summarized in Table 3. Using the fresh catalyst, 97% yield was obtained (run 1). The use of the recovered catalyst also produced an excellent yield of the coupling product (run 2, 98%). Again, the catalyst was recovered and used repeatedly. Even when the catalyst was reused for the 11th time, the coupling reaction of 4-bromoacetophenone with phenylboronic acid still proceeded smoothly to give the desired product in excellent yield (run 11, 96%), and the proportion of Pd on the recovered catalyst was 1.83 wt% determined by ICP analysis. When the catalyst was reused for the 12th time, a slightly reduced yield was obtained (run 12, 82%). These results clearly indicate that the microcapsule-supported palladium catalyst is very stable and can be used repeatedly.

3.4. Three-phase test

In an attempt to ascertain whether the catalysis occurred inside or outside of the microcapsules, a three-phase test was utilized (Scheme 2). This test, developed by Rebek and co-workers [22,23] and used by Corma [24,25], Davies [26], and others [27–29], is considered to be a definitive test for the presence of catalytically active homogeneous metal species. In our case, if the catalyst remains immobilized inside of the microcapsules, no transformation should be observed for the anchored aryl bromide, because the solid substrate could not enter the microcapsule through the pores of microcapsule to access the catalyst species. If homogeneous Pd is released outside of the microcapsules, then the supported aryl bromide can be converted to product, a biaryl compound. When the three-phase test was performed under standard conditions (K_2CO_3, $PhB(OH)_2$, IPA, 1.0 mol% Pd, 80 °C, 5 h), 4-bromobenzoic acid was recovered in 92% GC yield upon cleavage from the support, and its coupling product, 4-phenylbenzoic acid, was observed in only 4% GC yield, which was considered that due to the small amount

Table 3
Recycled use of the microcapsule-supported Palladium catalyst for Suzuki reaction of 4-bromoacetophenone with phenylboronic acid[a].



Run	Yield (%)[b]	Run	Yield (%)[b]
1	97	7	94
2	98	8	92
3	98	9	96
4	92	10	98
5	98	11	96
6	92	12	82

[a] *Reaction conditions:* 4-bromoacetophenone (0.5 mmol), phenylboronic acid (1.5 equiv.), K_2CO_3 (1.5 equiv.), 1 mol% Pd catalyst (12.5 mg), IPA (2 mL), 80 °C, 2 h.
[b] Isolated yield.

of leaching Pd. The coupling product, 4-biphenylcarboxamide, derivered from the soluble 4-bromobenzamide substrate was obtained in 92% isolated yield. These results clearly indicate that the microcapsule-supported Pd catalyst is very stable and almost all of the catalysis occurred inside of the microcapsules. Further evidence was provided by a hot filtration experimentation. After the supported catalyst was filtrated off from the hot reaction mixture, the desired Suzuki coupling reaction almost could not proceed under the same conditions.

4. Conclusions

In conclusion, we present a new method for the preparation of supported palladium catalyst for C–C bond forming reaction. In the microcapsule-supported palladium catalyst prepared, the Pd species were anchored inside of the microcapsules, which therefore acted as microreactors. It was considered that the substrates entered the microcapsule through its pores and were transformed to the products through the catalysis of the palladium immobilized within the microcapsule. The products then came back out through the pores. Our study on the catalyst reuse suggests that the microcapsule-supported palladium catalyst was very stable and can be reused at least 11 times without loss of catalytic activity. Further investigations of other reactions using the microcapsule-supported palladium catalyst as a catalyst are now in progress.

Acknowledgements

We are grateful to the National Natural Science Foundation of China (20572010) for financial support. This work was partly supported by the Program for Changjiang Scholars and Innovative Research Teams in Universities (IRT0711).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2010.02.029.

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