Preparation and application of SBA-15-supported palladium catalyst for Suzuki reaction in supercritical carbon dioxide

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The external and internal surfaces of SBA-15 were modified by $(MeO)_3SiPh$ and a phosphine ligand, $(MeO)_3SiCH_2CH_2CH_2SCH_2C_6H_4PPh_2$, before and after the template Pluronic P123 copolymer was removed, respectively. Palladium was then tethered within the cavity of the mesoporous material Ph-SBA-15-PPh_3 *via* a ligand-exchange reaction to provide a new supported palladium catalyst Ph-SBA-15-PPh_3-Pd. This catalyst was demonstrated to be a robust and active catalyst in Suzuki reaction of a wide range of aryl bromides with arylboronic acids in supercritical carbon dioxide. After the reaction mixtures were treated at 90 °C for 24 h, the crude coupling products were obtained as crystalline solids when the reaction temperature was lowered to room temperature and the carbon dioxide was then slowly released. The pure products can be obtained by simple recrystallization in good to excellent yields. The Ph-SBA-15-PPh_3-Pd catalyst has low leaching loss and can be reused at least 7 times without loss of activity.

Introduction

The Suzuki reaction of organoboron reagents with organic halides represents one of the most versatile and straightforward methods for the construction of new carbon–carbon bonds in the synthesis of fine chemicals, agrochemicals, and active pharmaceutical intermediates as well as functional materials.[1] It is well known that when the Suzuki reaction is performed in conventional organic solvent using a homogeneous palladium catalyst there are often some drawbacks: it is difficult to separate the coupling product from the catalyst and any organic solvent, the expensive palladium catalyst cannot be recycled, and the organic solvent could potentially cause environmental contamination due to its volatility. Green solvents, water,[2] ionic liquids,[3] and supercritical carbon dioxide,[4] have recently been used in Suzuki reactions to achieve environmentally benign processes. Furthermore, the Suzuki reactions have been successfully performed under solvent-free conditions.[5] To accomplish the recycled use of expensive palladium species, many heterogeneous palladium catalysts such as polymer-supported palladium catalysts,[6] SBA-15 or SBA-16/Pd,[7] and polyurea-encapsulated palladium catalyst[8] as well as others,[9] have been prepared for Suzuki reactions. In many cases, both the green solvent and heterogeneous palladium catalyst were used together in the Suzuki reaction. However, it has been clearly demonstrated that heterogeneous palladium catalysts act as reservoirs for highly active soluble forms of Pd in many cases, and this behavior may lead to the leaching of active catalyst species.

Crudden and co-workers have more recently reported excellent results.[7e] In their research thiol-modified mesoporous material (SBA-15-SH) was employed as a support for the preparation of the immobilized palladium catalyst (SBA-15-SH-Pd), which was found to be an active and stable catalyst for Suzuki reaction in water with virtually no leaching of Pd. The heterogeneity tests including hot filtration tests and three-phase tests have demonstrated that the catalysis occurs on the surface or in the pores of the silicate.

Inspired by the work of Crudden *et al.* as mentioned above, we attempted the Suzuki reaction of 1-bromo-4-nitrobenzene with phenylboronic acid utilizing the SBA-15-SH-Pd catalyst in supercritical carbon dioxide, and the desired coupling product, 4-nitrobiphenyl, was obtained in 60% yield under the optimized reaction conditions. This result indicated that SBA-15-supported palladium catalyst can be used in Suzuki reaction in supercritical carbon dioxide, and encouraged us to design and prepare a new SBA-15-supported palladium catalyst to increase the reaction yield. Prompted by the work of Kerton and co-workers,[9d] who demonstrated that polydimethylsiloxane-derived phosphine ligand (PDMS-PPh_2) based nanopalladium catalyst can be used in Suzuki reaction of 4-iodotoluene with phenylboronic acid in supercritical carbon dioxide to provide a coupling product in excellent yield, we prepared a new SBA-15-supported palladium catalyst. The principle of the preparation is illustrated in Scheme 1. At first, the external surface of SBA-15 was modified by $(MeO)_3SiPh$ before the template was removed, and the internal surface was then modified by a phosphine ligand, $(MeO)_3SiCH_2CH_2CH_2SCH_2C_6H_4PPh_2$, after the template was removed. Finally, palladium was tethered within the cavity of the mesoporous material Ph-SBA-15-PPh_3 *via* a ligand-exchange reaction. This newly formed SBA-15-supported palladium catalyst (Ph-SBA-15-PPh_3-Pd) may act as a nanoreactor, in which the catalysis will occur. Even if the palladium species breaks off from one phosphine ligand, it may attach to another phosphine ligand inside of the SBA-15. Therefore, the Ph-SBA-15-PPh_3-Pd catalyst should be very stable, and could be reused several times without loss of activity. As expected, the Ph-SBA-15-PPh_3-Pd catalyst exhibited high

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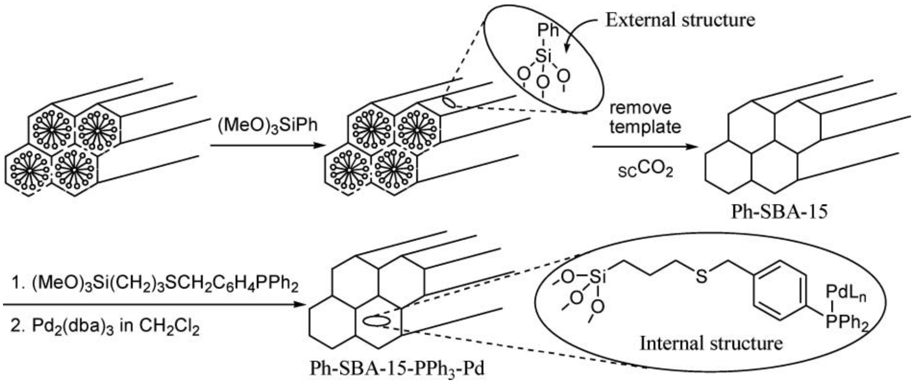


Scheme 1 Schematic illustration for the preparation of the SBA-15 supported palladium catalyst.

catalytic activity in Suzuki reaction of various aryl bromides with arylboronic acids in supercritical carbon dioxide. Here we wish to report our results.[10]

Results and discussion

Preparation and characterization of the catalyst Ph-SBA-15-PPh$_3$-Pd

According to the process as illustrated in Scheme 1, the mesoporous materials Ph-SBA-15 and Ph-SBA-15-PPh$_3$ as well as the desired catalyst Ph-SBA-15-PPh$_3$-Pd were synthesized. Fig. 1 shows the UV-visible spectra of the SBA-15 and Ph-SBA-15. Compared with SBA-15, Ph-SBA-15 has an obvious absorption peak of the benzene ring at 263 nm which revealed that the external surface of SBA-15 has been successfully modified with (MeO)$_3$SiPh.

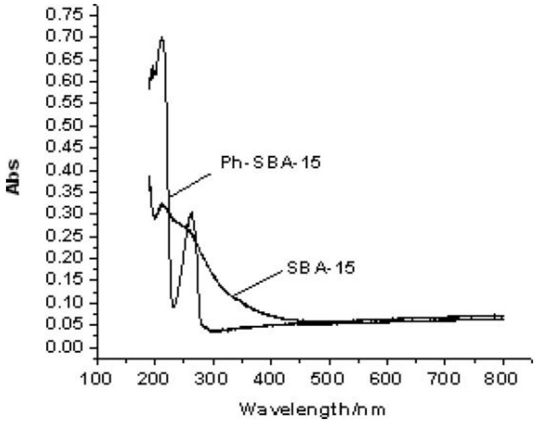


Fig. 1 UV-visible spectra of SBA-15 and Ph-SBA-15.

The N$_2$ sorption isotherms of Ph-SBA-15 and Ph-SBA-15-PPh$_3$-Pd are displayed in Fig. 2. Both materials exhibit a type-IV isotherm pattern with an H2 hysteresis loop, which is characteristic of the mesoporous structure. Although the mesoporous structure of the catalyst Ph-SBA-15-PPh$_3$-Pd was still maintained, the surface area and pore volume showed a significant decrease, which indicated that the ligand (MeO)$_3$SiCH$_2$CH$_2$CH$_2$SCH$_2$C$_6$H$_4$PPh$_2$ was introduced into the interior of Ph-SBA-15. Therefore the palladium species were immobilized on the modified internal surface of the mesoporous material. As shown in Fig. 3, the pore size distribution of catalyst Ph-SBA-15-PPh$_3$-Pd was very narrow. The average pore size of the catalyst Ph-SBA-15-PPh$_3$-Pd was *ca.* 5.2 nm calculated by Barrett–Joyner–Halenda (BJH) method.

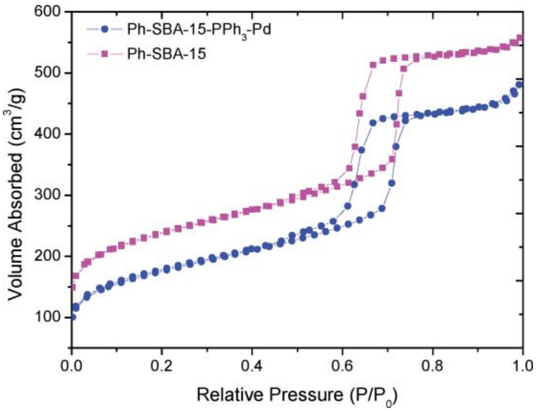


Fig. 2 N$_2$ adsorption-desorption isotherms for Ph-SBA-15 and Ph-SBA-15-PPh$_3$-Pd.

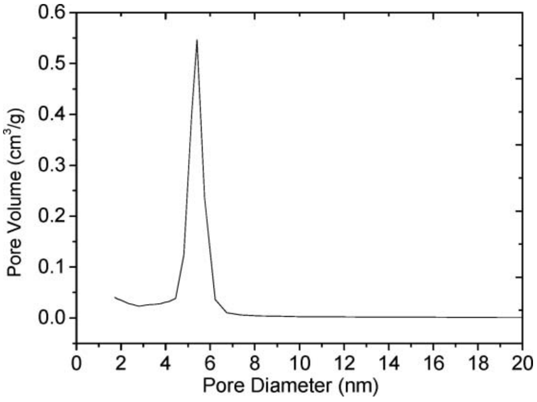


Fig. 3 Pore size distribution of catalyst Ph-SBA-15-PPh$_3$-Pd.

The ordered mesoporous structure of Ph-SBA-15, Ph-SBA-15-PPh$_3$, and Ph-SBA-15-PPh$_3$-Pd were further confirmed by the XRD pattern determination (Fig. 4). All the three curves obtained displayed an intense peak and two weak peaks, respectively, which matched well with the pattern of SBA-15 silica reported in the literature.[11] The prominent peaks should be indexed as (100) diffraction peaks, and the others as (110) and

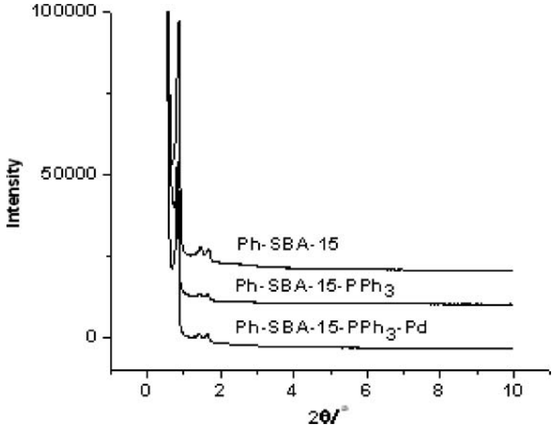


Fig. 4 XRD patterns of Ph-SBA-15, Ph-SBA-15-PPh$_3$, and Ph-SBA-15-PPh$_3$-Pd.

(200) diffraction peaks. After a phosphine ligand was introduced into the interior of Ph-SBA-15, the XRD pattern of parent SBA-15 silica is still kept very well. However, due to filling of the grafting organic functional groups in the pore of Ph-SBA-15, a decrease in the intensity of diffraction peaks is observed.

The scanning electron microscopy image (SEM) of catalyst Ph-SBA-15-PPh$_3$-Pd (Fig. 5) shows rope-like domains aggregating to wheat-head like macrostructures, similar to that of parent SBA-15, indicating that modification of external and internal surfaces does not influence the morphology of the mesoporous silica SBA-15. The transmission electron microscopy (TEM) shows well-ordered hexagonal pore channels in catalyst Ph-SBA-15-PPh$_3$-Pd (Fig. 6, upper). The TEM image also reveals arrays in catalyst Ph-SBA-15-PPh$_3$-Pd when viewed perpendicular to the channel axis (Fig. 6, lower).

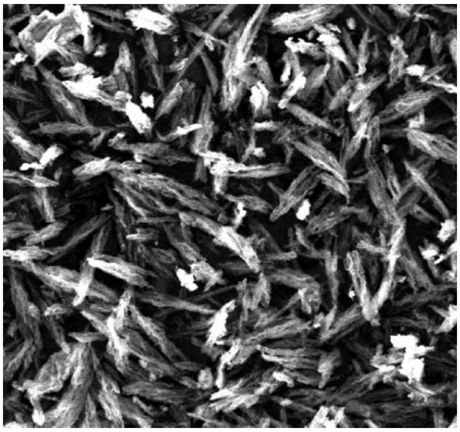


Fig. 5 SEM image of Ph-SBA-15-PPh$_3$-Pd.

Finally, inductively coupled plasma (ICP) analysis indicated that the ratio of Pd on the catalyst Ph-SBA-15-PPh$_3$-Pd was 1.04 wt%.

Suzuki coupling reaction catalyzed by Ph-SBA-15-PPh$_3$-Pd

The Suzuki cross-coupling reaction between aryl bromides and arylboronic acids was chosen to evaluate the catalytic activity and stability of the catalyst Ph-SBA-15-PPh$_3$-Pd in supercritical carbon dioxide.[12,13] The influences of base and catalyst loading in the model reaction of 1-bromo-4-nitrobenzene with phenylboronic acid were first investigated, and the results of which are shown in Table 1. Among the bases examined, $K_3PO_4 \cdot 3H_2O$ gave the best result (99% yield, entry 7). The other bases including organic bases and inorganic bases, such as diisopropyl ethyl amine (DIPEA), $MeCO_2NBu_4$, NEt_3, $MeCO_2K$, and KOH, gave low to moderate yields or no reaction (entries 1–6 and 8–11). When the Pd loading was decreased from 0.8 mol% to 0.6 mol%, a decreased reaction yield was obtained (87%, entry 12). Therefore, $K_3PO_4 \cdot 3H_2O$ was employed as a base and the 0.8 mol% of Pd loading was chosen in the subsequent study.

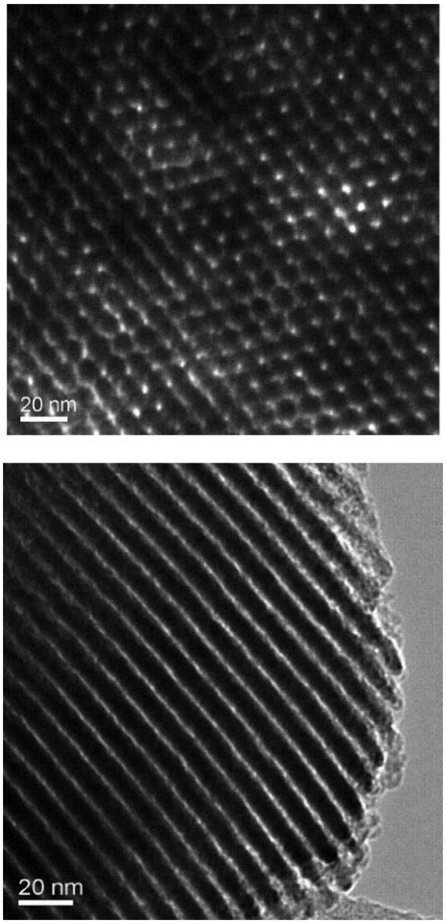
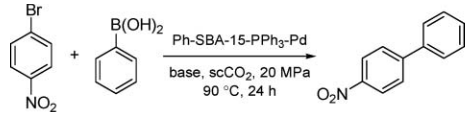


Fig. 6 TEM image of Ph-SBA-15-PPh$_3$-Pd: (upper) taken along the parallel channels; (lower) vertical to the parallel channels.

Suzuki reactions of a wide range of aryl bromides with arylboronic acids were tested, the catalysis results of which are summarized in Table 2. The reactions of aryl bromides bearing electron-withdrawing groups such as NO_2, CH_3CO, and CHO at the *para* position, respectively, with phenylboronic acid proceeded smoothly to furnish biphenyls in good to excellent yields (84–99%, entries 1–3). Even aryl bromide bearing OH, an electron-donating group, at the *para* position, the coupling reaction of which with phenylboronic acid gave also excellent yield (95%, entry 4). 3-Bromopyridine, a brominated aromatic heterocycle, was also treated with phenylboronic acid, and 61% reaction yield was obtained (entry 5, 3-bromopyridine was recovered in 23% yield). Finally, the MeO or F substituted arylboronic acid was employed in the coupling reaction of

Table 1 Effects of base and catalyst loading on the Suzuki coupling reaction of 1-bromo-4-nitrobenzene with phenylboronic acid catalyzed by Ph-SBA-15-PPh$_3$-Pd in supercritical carbon dioxide[a]



Entry	Base	Pd (mol%)	Yield (%)[b]
1	DIPEA	0.8	58
2	$MeCO_2NBu_4$	0.8	56
3	NEt_3	0.8	47
4	K_2CO_3	0.8	49
5	$K_3PO_4\cdot 7H_2O$	0.8	55
6	K_3PO_4	0.8	18
7	$K_3PO_4\cdot 3H_2O$	0.8	99
8	$K_3PO_4\cdot H_2O$	0.8	9
9	KOH	0.8	NR[c]
10	NaF	0.8	NR[c]
11	$MeCO_2K$	0.8	16
12	$K_3PO_4\cdot 3H_2O$	0.6	87

[a] Reaction conditions: 1-bromo-4-nitrobenzene (0.5 mmol), phenylboronic acid (1.5 equiv.), base (2.0 equiv.), Ph-SBA-15-PPh$_3$-Pd (Pd: 0.6-1.0 mol%), scCO$_2$, 90 °C, 20 MPa, 24 h. [b] Isolated yields. [c] No reaction.

1-bromo-4-nitrobenzene. The reaction of 1-bromo-4-nitrobenzene with 4-methoxyphenylboronic acid also proceeded smoothly to offer the desired biaryl in 91% yield (entry 6). High yields were obtained from the reactions of 1-bromo-4-nitrobenzene with 4-fluorophenylboronic acid or 3,4-difluorophenylboronic acid (83% and 86%, respectively, entries 7 and 8). Except for the 3,4-difluoro-4′-nitro-1,1′-biphenyl[14] in entry 8, other coupling products are known compounds and their ^{1}H NMR data were consistent with those reported in the literature.[15–19]

Interestingly, after the reaction mixtures were treated at 90 °C for 24 h, the crude coupling products were obtained as crystalline solids in all cases when the reaction temperature was lowered to room temperature and the carbon dioxide was then slowly released. And the pure products could be obtained by simple recrystallization in good to excellent yields. Fig. 7 shows the crystalline state and ^{1}H-NMR spectrum of crude and pure coupling product, 4-acetylbiphenyl. Compared with the ^{1}H-NMR spectrum of pure 4-acetylbiphenyl (Fig. 7, right), the ^{1}H-NMR spectrum of crude 4-acetylbiphenyl (Fig. 7, left) indicated that the crude product has fairly high purity.

The stability of the catalyst Ph-SBA-15-PPh$_3$-Pd 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, 96%). Again, the catalyst was recovered and used repeatedly. Even when the catalyst was reused for the seventh time, the coupling reaction of 4-bromoacetophenone with phenylboronic acid still proceeded smoothly to give the desired product in excellent yield (run 7, 96%). Extremely low leaching of the catalyst is observed, at the end of the reaction only 0.009% of the initially added Pd was lost, as determined by ICP analysis. These results clearly

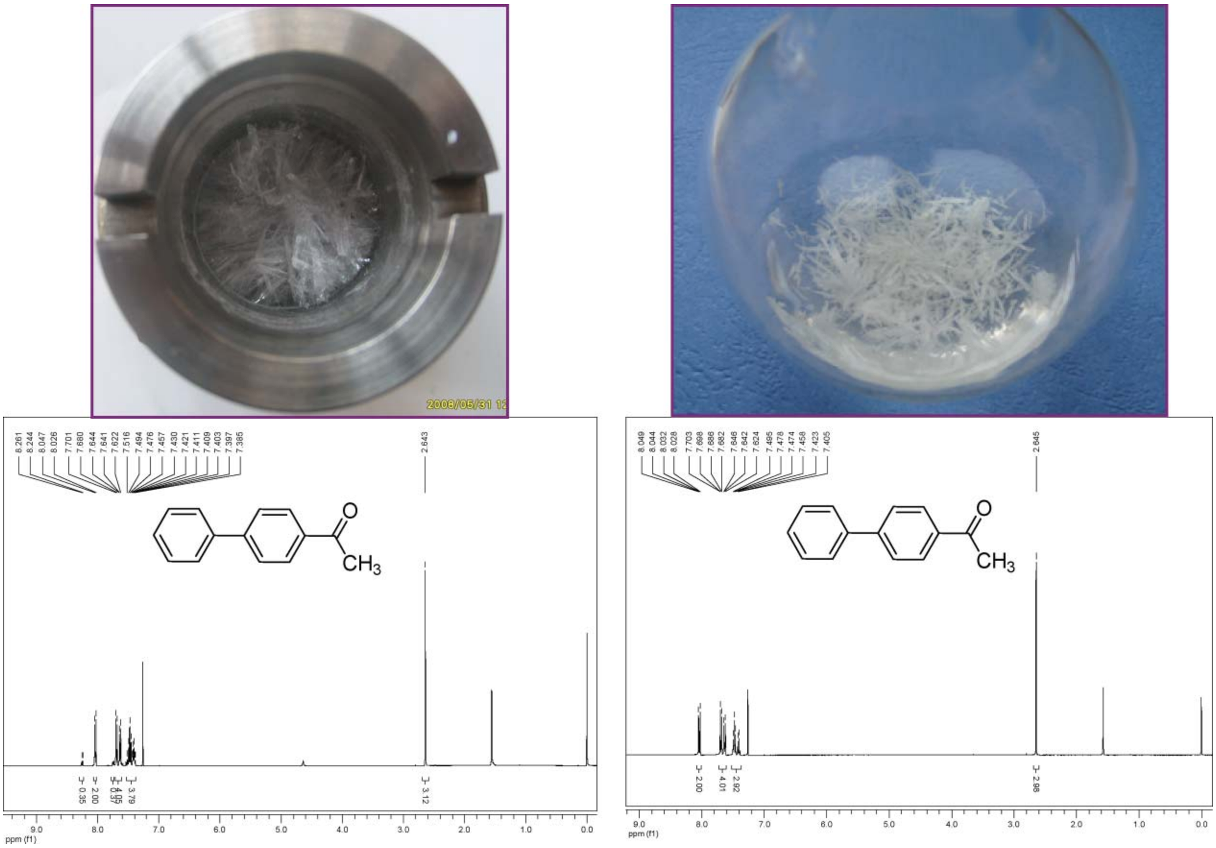
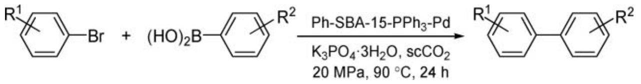
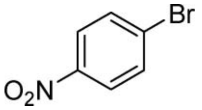
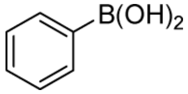
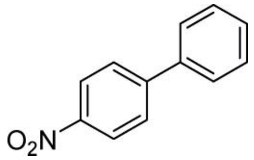
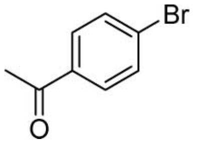
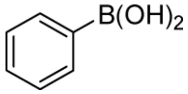
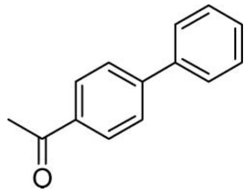
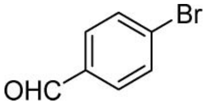
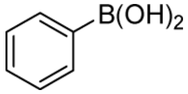
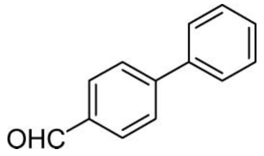
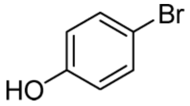
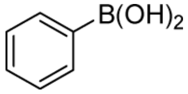
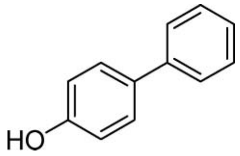
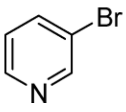
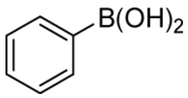
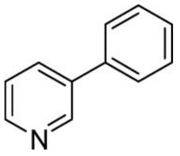
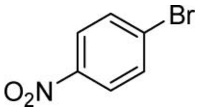
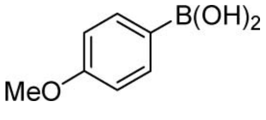
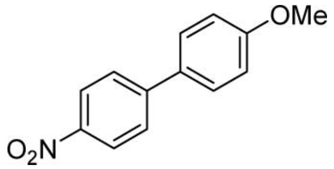
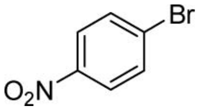
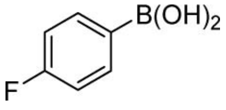
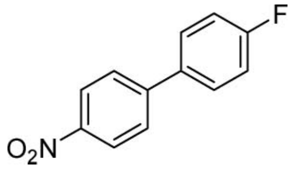
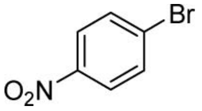
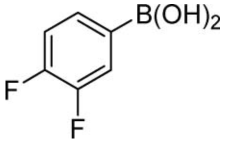
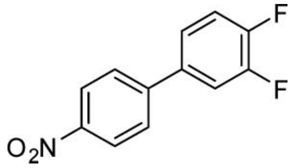


Fig. 7 (Left) Crystalline state and ^{1}H NMR spectrum of crude 4-acetylbiphenyl. (Right) Crystalline state and ^{1}H NMR spectrum of pure 4-acetylbiphenyl.

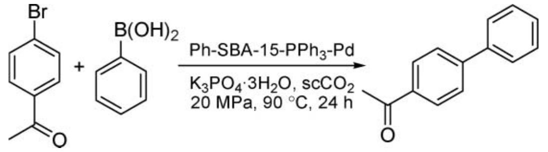
Table 2 Suzuki coupling reaction of aryl bromides with arylboronic acids catalyzed by Ph-SBA-15-PPh$_3$-Pd[a]



Entry	Aryl bromide	Arylboronic acid	Product	Yield (%)[b]
1				99
2				97
3				84
4				95
5				61[c]
6				91
7				83
8				86

[a] Reaction conditions: aryl bromides (0.5 mmol), arylboronic acids (1.5 equiv.), $K_3PO_4 \cdot 3H_2O$ (2.0 equiv.), Ph-SBA-15-PPh$_3$-Pd (Pd: 0.8 mol%), scCO$_2$, 90 °C, 20 MPa, 24 h. [b] Isolated yields. [c] 3-Bromopyridine was recovered in 23% yield.

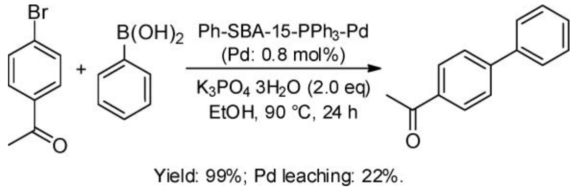
Table 3 Recycled use of the Ph-SBA-15-PPh_3-Pd catalyst for Suzuki reaction of 4-bromoacetophenone with phenylboronic acid[a]



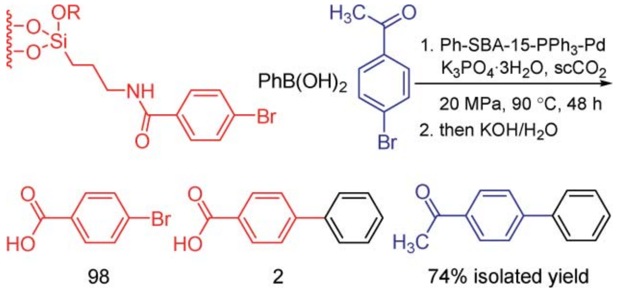
Run	Yield (%)[b]	Run	Yield (%)[b]
1	97	5	97
2	96	6	97
3	98	7	96
4	99		

[a] Reaction conditions: 4-Bromoacetophenone (0.5 mmol), phenylboronic acid (1.5 equiv.), $K_3PO_4{\cdot}3H_2O$ (2.0 equiv.), Ph-SBA-15-PPh_3-Pd (Pd: 0.8 mol%), $scCO_2$, 90 °C, 20 MPa, 24 h. [b] Isolated yields.

indicate that this catalyst Ph-SBA-15-PPh_3-Pd is very stable and can be used repeatedly without loss of activity. In addition, as a comparative test, we examined the cross-coupling reaction of 4-bromoacetophenone with phenylboronic acid using catalyst Ph-SBA-15-PPh_3-Pd in ethanol, and found that the desired cross-coupling product was also obtained in excellent yield (99%). However, the Pd leaching of the catalyst (22%) in ethanol is much larger than that in supercritical CO_2 (Scheme 2).



Scheme 2 Cross-coupling reaction of 4-bromoacetophenone with phenylboronic acid catalyzed by Ph-SBA-15-PPh_3-Pd in ethanol.



Scheme 3 Three-phase test in the Suzuki reaction with catalyst Ph-SBA-15-PPh_3-Pd.

In an attempt to ascertain whether the catalysis occurred inside or outside of the catalyst Ph-SBA-15-PPh_3-Pd, a three-phase test was utilized (Scheme 3). This test, developed by Rebek and co-workers[20] and used by Corma,[21] Davies,[22] and others,[7e,23] 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 mesoporous materials, no transformation should be observed for the anchored aryl bromide, because the solid substrate could not enter the cavities of the mesoporous materials to access the catalyst species. If homogeneous Pd is released outside of the mesoporous material, then the supported aryl bromide can be converted to produce a biaryl compound. When the three-phase test was performed under standard conditions ($K_3PO_4{\cdot}3H_2O$, $PhB(OH)_2$, $scCO_2$, 0.8 mol% Pd, 90 °C, 48 h), 4-bromobenzoic acid was recovered in almost quantitative yield upon cleavage from the support, and its coupling product, 4-phenylbenzoic acid, was obtained in trace level, which was considered that due to the small amount of leaching Pd. The coupling product, 4-phenylacetophenone, derived from the soluble 4-bromoacetophenone substrate was obtained in 74% isolated yield. These results clearly indicate that the catalyst Ph-SBA-15-PPh_3-Pd is very stable and almost all of the catalysis occurred inside of the mesoporous material.

Conclusions

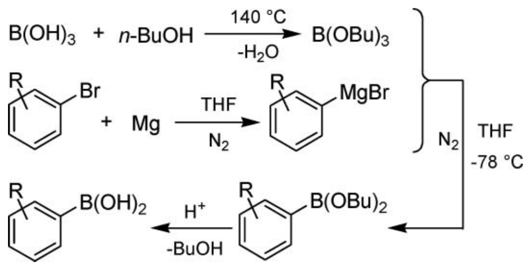
In conclusion, we present a new method for the preparation of SBA-15-supported palladium catalyst (Ph-SBA-15-PPh_3-Pd) for the Suzuki coupling reaction in supercritical carbon dioxide. In the prepared catalyst Ph-SBA-15-PPh_3-Pd, the Pd species were anchored inside of the mesoporous materials, which therefore acted as nanoreactors. Our study on the catalyst reuse suggests that the catalyst Ph-SBA-15-PPh_3-Pd was very stable and can be reused at least 7 times without loss of catalytic activity. The high catalytic activity of Ph-SBA-15-PPh_3-Pd may be attributed to the flexible chain between the triphenylphosphine ligand and SBA-15, which could make the catalysis of supported palladium species is similar to those of a homogeneous catalyst. The use of supercritical carbon dioxide as a green solvent not only prevents potential environmental contamination, but also prevents the leaching of the Pd species from their support. Further investigations of other C–C bond forming reactions using Ph-SBA-15-PPh_3-Pd as a catalyst are now in progress.

Experimental

Reagents and materials

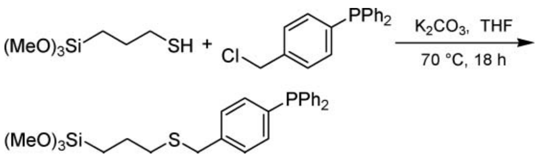
Pluronic P123 copolymer ($EO_{20}PO_{70}EO_{20}$) and 1-bromo-4-nitrobenzene were purchased from Sigma-Adrich Company. Tetraethylorthsilicate (TEOS) was obtained from Beijing Chemical Reagents Company, China. $Pd_2(dba)_3$ was purchased from Shanghai Zealandchem Co., Ltd., China. Trimethoxyphenylsilane, 4-bromobenzaldehyde, 4-methylbenzenesulfonic acid, chlorodiphenylphosphine, and KBH_4 were obtained from Shanghai Chemical Reagent Company of Chinese Medicine Group. 3-(Trimethoxysilyl)propane-1-thiol, bromobenzene, 4-bromotoluene, 1-bromo-4-fluorobenzene, 1-bromo-3,4-difluorobenzene, and 4-bromoanisole were obtained from ABCR GmbH & Co. KG, Germany. 4-Bromoacetophenone was purchased from Alfa Aesar China (Tianjin) Co., Ltd. 4-Bromophenol and 3-bromopyridine were purchased from Acros Organics.

The arylboronic acids including phenylboronic acid, 4-methoxyphenylboronic acid, 4-fluorophenylboronic acid, and 3,4-difluorophenylboronic acid were synthesized from the corresponding aryl bromides (bromobenzene, 4-bromoanisole, 1-bromo-4-fluorobenzene, and 1-bromo-3,4-difluorobenzene) according to the modified method (Scheme 4).[24] A solution of an arylmagnesium bromide (0.2 mol, in 80 mL of THF) was added dropwise to a solution of *n*-butyl borate (0.2 mol) in 80 mL of dry THF at −78 °C under nitrogen atmosphere with vigorous stirring. The resulting mixture was continuously stirred for 3 h at the same temperature of −78 °C. Then the reaction mixture was allowed to warm slowly to room temperature. After the reaction mixture was continuously stirred for 10 h at room temperature, an aqueous solution of HCl (6 wt%) was added dropwise until the pH of the mixture was reduced to *ca.* 5. The resulting mixture was filtered under reduced pressure, and then the filtrate obtained was extracted with ether (50 mL × 3). The extracts were combined, and evaporated to remove ether, THF, and *n*-BuOH to obtain a crude arylboronic acid. The recrystallisation of crude arylboronic acids from water afforded pure arylboronic acids as white needle crystals in 42–64% yields.



Scheme 4 Preparation of arylboronic acids.

Ligand $(MeO)_3SiCH_2CH_2CH_2SCH_2C_6H_4PPh_2$ was synthesized as described below (Scheme 5). A mixture of K_2CO_3 (2.0 g 14.5 mmol), 3-(trimethoxysilyl)propane-1-thiol (1.8 mL, 10 mmol), and THF (20 mL) was stirred at 70 °C for 2 h, and then to which a solution of (4-(chloromethyl)-phenyl)diphenylphosphine[25] (3.7 g, 12 mmol) in THF (30 mL) was added dropwise. The resulting mixture was continuously stirred at 70 °C for 18 h, then the mixture was cooled to room temperature and filtered to remove solid inorganic salts, and the filtrate was evaporated to remove solvent under reduced pressure. Pure $(MeO)_3SiCH_2CH_2CH_2SCH_2C_6H_4PPh_2$ was obtained as a colorless viscous liquid (2.2 g, 48%) by a chromatography on silica gel column [petroleum ether (60–90 °C)/ethyl acetate = 10 : 1]. ^1H NMR (400 MHz, $CDCl_3$): δ 0.72 (t, J = 8.2 Hz, 2H), 1.66–1.70 (m, 2H), 2.45 (t, J = 7.4 Hz, 2H), 3.54 (s, 9H), 3.68 (s, 2H), 7.23–7.32 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 8.7, 22.7, 34.5, 36.0, 76.9, 77.2, 77.5, 128.6, 128.7, 128.8, 129.1, 129.2, 133.7, 133.9, 134.1, 137.3, 137.4, 139.5; ^{31}P NMR (161 MHz, EtOAc): δ −8.63; HRMS (EI) calcd for $C_{25}H_{31}O_3PSSi$: 470.1501 $[M]^+$; found: 470.1511.



Scheme 5 Synthesis of phosphine ligand having $(MeO)_3Si$ moiety.

Preparation of mesoporous material Ph-SBA-15-PPh$_3$

Mesoporous material Ph-SBA-15-PPh$_3$ was synthesized according to the modified method (Scheme 1).[26] A mixture of Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, 4.0 g), diluted HCl solution (6 wt%, 120 g), and deionized water (30 mL) was stirred at room temperature until the template Pluronic P123 was dissolved completely. After the temperature of the resulting solution was increased to 40 °C, 8.4 g of tetraethylorthsilicate was added dropwise to the solution. After being stirred for 24 h, the resultant suspension was transferred into an autoclave. The autoclave was placed under static conditions at 100 °C for 24 h. After the temperature was reduced to room temperature, the precipitated solid was isolated by a filtration, washed with deionized water (100 mL) and ethanol (25 mL) successively, and dried at 80 °C under vacuum for 5 h.

The solid (2.0 g) obtained was treated with trimethoxyphenylsilane (2.0 mL) in toluene (50 mL) in the presence of pyridine (2.0 mL) at 115 °C for 2 h. After the mixture was cooled to room temperature, the precipitated white solid was isolated by filtration, washed with ethanol, ethyl ether, and acetone successively, and dried at 80 °C under vacuum for 5 h. Then the template Pluronic P123 was removed by extraction with supercritical carbon dioxide to obtain the mesoporous material Ph-SBA-15.[27]

The mesoporous material Ph-SBA-15 (1.5 g) obtained was treated with ligand $(MeO)_3SiCH_2CH_2CH_2SCH_2C_6H_4PPh_2$ (1.5 g) in toluene (80 mL) in the presence of pyridine (1.5 mL) at reflux under N_2 atmosphere for 24 h. The mixture was slowly cooled to room temperature, and then the precipitated white solid was isolated by a filtration, washed with methanol, ethyl ether, acetone, and hexane successively, and dried at 80 °C under vacuum for 5 h. The mesoporous material Ph-SBA-15-PPh$_3$ was eventually obtained as white solid powders.

Preparation of catalyst Ph-SBA-15-PPh$_3$-Pd

Mesoporous materials Ph-SBA-15-PPh$_3$ (1.0 g) was treated with a solution of $Pd_2(dba)_3$ (0.1 g) in CH_2Cl_2 (50 mL) at room temperature under N_2 atmosphere for 24 h. Such palladium species were tethered within the cavity of the mesoporous materials Ph-SBA-15-PPh$_3$ *via* a ligand-exchange reaction. The content of Pd in the mesoporous materials was determined by ICP after the resultant khaki solid was filtrated and washed with CH_2Cl_2 (10 mL×2) as well as dried at 80 °C under vacuum for 2 h.

General procedure for Suzuki coupling reaction

The supported catalyst Ph-SBA-15-PPh$_3$-Pd (0.8 mol% Pd), aryl bromide (0.5 mmol), arylboronic acid (0.75 mmol, 1.5 equiv.), and $K_3PO_4 \cdot 3H_2O$ (1.0 mmol, 2 equiv.) were placed in a 25 mL stainless steel pressure vessel with a magnetic stir bar under nitrogen atmosphere. The vessel was purged with carbon dioxide three times, and then 15 g of carbon dioxide was filled into the vessel. It was then heated to 90 °C for 24 h. The pressure increased to 20 MPa at this temperature. The vessel was allowed to cool to room temperature and was then vented into ethyl acetate (30 mL). The resultant crystalline solid (crude coupling product) was purified by a simple recrystallization process. The catalyst Ph-SBA-15-PPh_3-Pd was collected, washed with water, ethanol and dichloromethane, then dried in a vacuum and reused.

Three-phase test

Silica gel supported aryl bromide was prepared according to the literature procedure.[7d] 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^{-1} determined by elemental analysis.

A mixture of 4-bromoacetophenone (0.25 mmol), phenylboronic acid (0.38 mmol, 1.5 equiv.), $K_3PO_4 \cdot 3H_2O$ (0.38 mmol, 1.5 equiv), silica gel supported aryl bromide (192 mg), catalyst Ph-SBA-15-PPh_3-Pd (0.8 mol% Pd), and carbon dioxide (15 g) in a 25 mL stainless steel pressure vessel was treated at 90 °C for 48 h. And then the mixture was allowed to cool to room temperature. 15 mL of ethyl acetate was added into the vessel to dissolve the coupling product, 4-phenylacetophenone, derived from the soluble 4-bromoacetophenone substrate. The resulting mixture was filtered, and the filtrate was evaporated to remove solvent under reduced pressure. Pure 4-phenylacetophenone was obtained in 74% isolated yield by a chromatography on silica gel column [petroleum ether (60–90 °C)/ethyl acetate = 20 : 1]. The separated solid was washed with ethanol, and further extracted with dichloromethane, and 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 ^1H NMR.

General characterization

UV-vis absorption spectrum was performed on the HP 8453 ultraviolet and visible spectrophotometry. N_2 physical adsorption was carried out on a Micrometrics ASAP2020 volumetric adsorption analyzer (before the measurements, samples were degassed at 433 k for 6 h). 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 $P/P0$ (above 0.99). Pore diameters were determined from the adsorption branch using Barrett–Joyner–Halenda (BJH) method. X-Ray diffraction (XRD) patterns were measured on a D/Max-2400 diffractometer using Cu-Kα-ray radiation (λ = 1.5405 Å) operating at 40 kV and 100 mA. The scanning electron microscopy (SEM) images were obtained using a JSM-5600LV microscope and transmission electron microscopy (TEM) with a Tecnai 20 microscope. The amount of Pd was obtained by inductively coupled plasma (ICP) atomic emission spectrometry (Optima 2000 DV). ^1H, ^{13}C, and ^{31}P NMR spectra were recorded in $CDCl_3$ or ethyl acetate solution on a Varian Inova-400 spectrometer (400 MHz for ^1H, 100 MHz for ^{13}C, 161 MHz for ^{31}P). The chemical shifts are reported in ppm downfield (δ) from Me_4Si. High resolution mass spectra were recorded on a Q-TOF mass spectrometry (Micromass, England) equipped with Z-spray ionization source.

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