Palladium-guanidine complex immobilized on SBA-16: a highly active and recyclable catalyst for Suzuki coupling and alcohol oxidation†

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By immobilizing a mixture of a palladium-guanidine complex and guanidine on the mesoporous cage-like material SBA-16 *via* a one-pot silylation, we have successfully prepared a new solid catalyst for Suzuki coupling and the aerobic oxidation of alcohols. The structure and composition of the solid catalyst were characterized with N_2 sorption, XRD, TEM, FT-IR and solid state NMR. The coordination state of the palladium-guanidine complex supported on the solid catalyst was preliminarily investigated with XPS and UV-vis spectroscopy. This catalyst afforded fast conversions for the Suzuki coupling of various aryl bromides and arylboronic acids in a 50% aqueous ethanol solution at 50 °C even at loadings of 0.01–0.001 mol%, and the TOF (turn-over frequency) for the Suzuki coupling of bromobenzene and arylboronic acids could be up to 45 700 h^{-1} under mild conditions. A satisfactory yield was obtained even after the catalyst was reused several times. The developed solid catalyst combined with the mild conditions investigated represents one of the most efficient heterogeneous systems for the Suzuki coupling of bromides. Furthermore, it was found that the solid catalyst could also work well for the aerobic oxidation of benzylic alcohols and cinnamyl alcohol, affording over 99% selectivity. The catalyst could be reused 15 times without a significant decrease in activity and selectivity.

Introduction

Pd-catalyzed reactions, such as Suzuki coupling and alcohol oxidation, are of significant importance in modern chemical transformations.[1] Various palladium complex catalysts for these reactions have been successfully established.[2] These metal complexes, however, suffer from practical problems such as catalyst separation, catalyst recycling and product contamination. To address these problems, palladium complexes as well as Pd nanoparticles have been immobilized on various supports such as silica, alumina, zeolites, organic polymers and dendrimers to create heterogeneous catalysts because these heterogeneous systems are easy to handle, recover and are "green" processes.[3] Although significant efforts and advances have been made along this line, the development of highly recyclable and active heterogeneous catalytic systems that could work well under mild conditions still remains a major challenge in view of the practical applications.

Our previous investigations and other groups' reports revealed that it was possible to improve the recyclability and activity of the immobilized catalyst by choosing a suitable support and ligand to be grafted on the support.[4] For both the Suzuki coupling and alcohol oxidation, it was found that the supported molecular catalysts were converted to palladium nanoparticles as the reaction proceeded.[3g,4a,5] Driven by the high surface energy, the palladium nanoparticles on the support are prone to aggregate and agglomerate into less active larger particles, and the recyclability of the immobilized catalyst was thus discounted. Accordingly, limiting the growth of Pd naonoparticles into the less active larger particles (even Pd black) is one of the key factors for improving the recyclability. Among various supports for efficiently preventing the growth of metal nanoparticles, mesoporous materials are very promising because of their regularly arranged pore structure on a mesoscopic scale. More interestingly, different to the widely used channel-like mesoporous materials MCM-41 and SBA-15, the recently synthesized SBA-16 (cubic, *Im*3*m*) is one of the new ordered mesoporous materials with cage-like structures.[6] This mesoporous cage-like material has tunable cage sizes (4–10 nm) and pore entrance sizes (generally less than 4 nm). The isolated nanocages are three-dimensionally interconnected by the pore entrances. Such isolated nanocages of SBA-16 could not only accommodate metal complexes and particles formed *in situ* during the catalytic reaction, but also limit the growth of metal nanoparticles by the spatial restrictions. Meanwhile, the smaller pore entrances may inhibit the motion of metal nanoparticles, thereby preventing undesired agglomeration. In our very recent study, it has been demonstrated that the cage-like SBA-16 exhibited a much better capability to prevent the growth of metal nanoparticles than the channel-like SBA-15 as well as amorphous silica, and the recyclability of the complex catalyst immobilized on SBA-16 was significantly improved.[4a]

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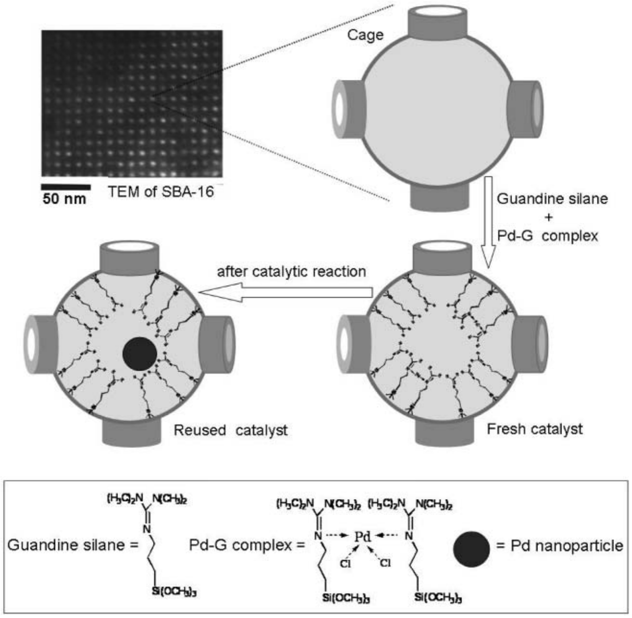
Recently, a palladium-tetramethylguanidine complex was found to be active in the Suzuki reaction.[7] Compared with the well-established phosphine, *N*-heterocyclic carbene and palladacyclic complex system, the palladium-guanidine complex is air-stable, inexpensive, has low toxicity and is easily accessible *via* chemical synthesis. Such advantages could make guanidine a potential ligand for practical applications. However, to the best of our knowledge, there has been no report about the heterogeneous palladium-guanidine complex catalyst.

This work aims to develop a more active and recyclable heterogeneous catalyst for Suzuki coupling and the aerobic oxidation of alcohols. By grafting a mixture of the palladium-guanidine complex and guanidine on SBA-16 *via* a one-pot silylation, we have successfully prepared a new solid catalyst. This catalyst afforded fast conversions for the Suzuki couplings of various aryl bromides and arylboronic acids in an aqueous ethanol solution at 50 °C even at catalyst loadings of 0.01–0.001 mol%. The turnover frequency (TOF) for the Suzuki coupling of bromobenzene and phenylboronic acid could be up to 45 700 h^{-1} under mild conditions. Furthermore, it was found that the solid catalyst could also work well for the aerobic oxidation of alcohols with over 99% selectivity.

Results and discussion

Catalyst preparation and characterization

The process for the preparation of the catalyst Pd-G/SBA-16-G is schematically depicted in Scheme 1. To form a covalent linkage with the mesoporous cage-like material SBA-16, tetramethylguanidine was first subjected to a derivation with chloropropyltrimethoxysilane, leading to 1,1,3,3-tetramethyl-2-(3-trimethoxysilylpropyl)-guanidine (G), as described in the Experimental. Then, an excess of G was coordinated with $PdCl_2$, resulting in a G solution containing the Pd-G complex. The Pd-G complex and residual G in this solution were grafted onto SBA-16 through a one-pot silylation. After being thoroughly washed with organic solvents, a solid catalyst denoted as Pd-G/SBA-16-G was obtained. The Pd content of the catalyst Pd-G/SBA-16-G, determined by ICP-AES, is 0.86 wt%. The N and C contents of the catalyst Pd-G/SBA-16-G determined by combustion chemical analysis are 3.58 wt% and 9.28 wt%, respectively. The determined atom ratios of Pd, C and N on the solid catalyst were, broadly, in agreement with the ratios expected.



Scheme 1 Schematic descriptions for preparing the solid catalyst Pd-G/SBA-16-G and the model for the reused catalyst.

In order to obtain the structural information about the solid catalyst on a mesoscopic scale, N_2 sorption and powder X-ray diffraction (XRD) were used to characterize Pd-G/SBA-16-G. The N_2 sorption isotherms and pore size distribution plots for SBA-16 and Pd-G/SBA-16-G, are displayed in Fig. 1 and Fig. 2, respectively. The textural parameters determined by the N_2 sorption are listed in the ESI, Table S1.† SBA-16 exhibits a type-IV isotherm pattern with an H2 hysteresis loop, which is characteristic of the mesoporous cage-like structure. Similar to the parent material SBA-16, Pd-G/SBA-16-G also shows a type-IV isotherm with an H2 hysteresis loop, indicating that the catalyst Pd-G/SBA-16-G still maintains a good mesoporous cage-like structure. It is worthwhile to note that the specific surface area, pore volume and pore size of the parent SBA-16

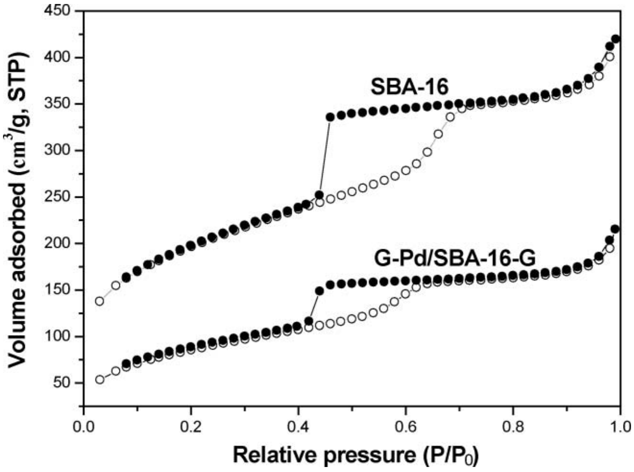


Fig. 1 N_2 sorption isotherms of SBA-16 and Pd-G/SBA-16-G.

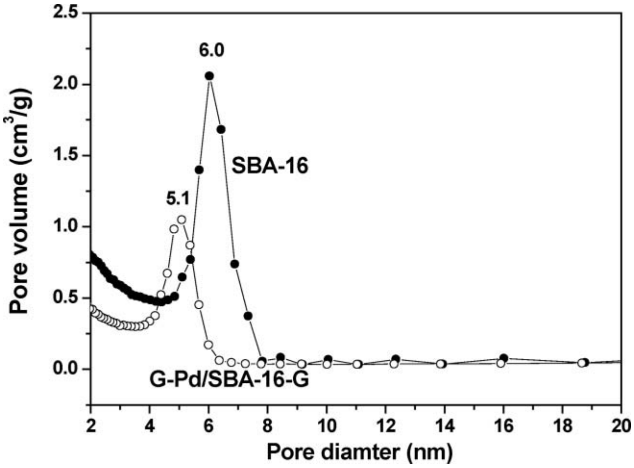


Fig. 2 Pore size distributions of SBA-16 and Pd-G/SBA-16-G.

undergo a significant decrease after grafting the mixture of the Pd-G complex and G (ESI, Table S1).† The significant decrease in these textural parameters may point out a fact that the Pd-G complex and G were introduced into the interior of SBA-16, as expected. The XRD patterns of SBA-16 and Pd-G/SBA-16-G are displayed in the ESI, Fig. S1.† Like the parent material SBA-16, Pd-G/SBA-16-G also shows a strong diffraction peak at small angles, further confirming that the periodic mesoporous structure of SBA-16 remained roughly intact during the course of preparing the catalyst.

The composition of the catalyst Pd-G/SBA-16-G was determined by FT-IR and solid state NMR. The FT-IR spectra of SBA-16 and Pd-G/SBA-16-G are shown in Fig. 3. Compared with the FT-IR spectrum of the parent material SBA-16, the FT-IR spectrum of Pd-G/SBA-16-G clearly exhibited three new peaks at 2943, 1590 and 1410 cm^{-1}, which correspond to the stretching vibrations of the C–H and C=N, and the bending vibration of C–H, respectively. Meanwhile, the intensity of the peak at 960 cm^{-1} (related to the bending vibration of Si–OH on SBA-16) significantly decreases after grafting with Pd-G complex and G. This can be explained by a fact that the Si–OH groups on the SBA-16 surface were consumed due to the silylation. These results indicate that the Pd-G complex and G were successfully immobilized on SBA-16. Fig. 4 and Fig. 5 show the ^{29}Si MAS NMR and ^{13}C CP-MAS NMR spectra of Pd-G/SBA-16-G, respectively. In Fig. 4, the solid state NMR spectrum of Pd-G/SBA-16-G shows a "T^3" band at *ca.* −63 ppm, indicating that the Pd-G complex and G were immobilized on SBA-16 through a condensation reaction of the surface silanols with silane derivatives. In Fig. 5, the carbon chemical shifts for the catalyst Pd-G/SBA-16-G are broadly in agreement with those values for G in solution (liquid state NMR, see Experimental).

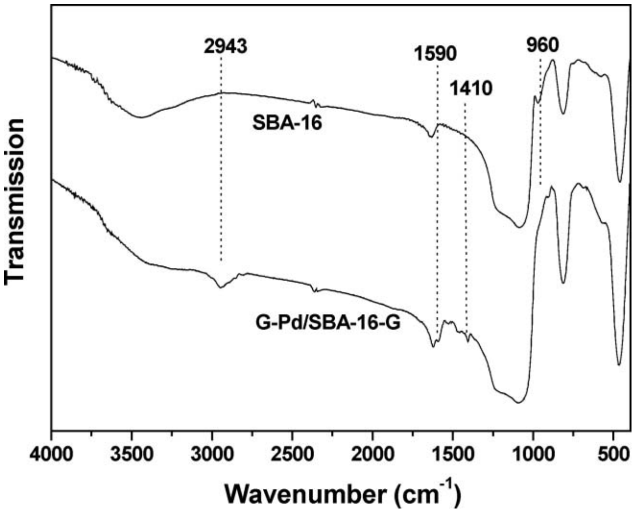


Fig. 3 FT-IR spectra of SBA-16 and G-Pd/SBA-16-G.

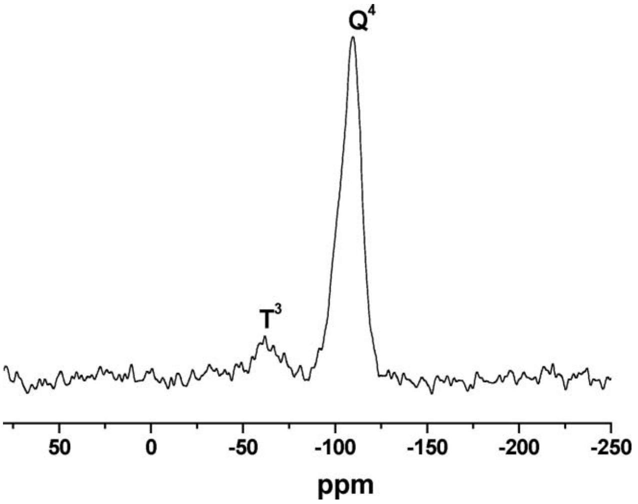


Fig. 4 ^{29}Si MAS NMR spectrum of G-Pd/SBA-16-G.

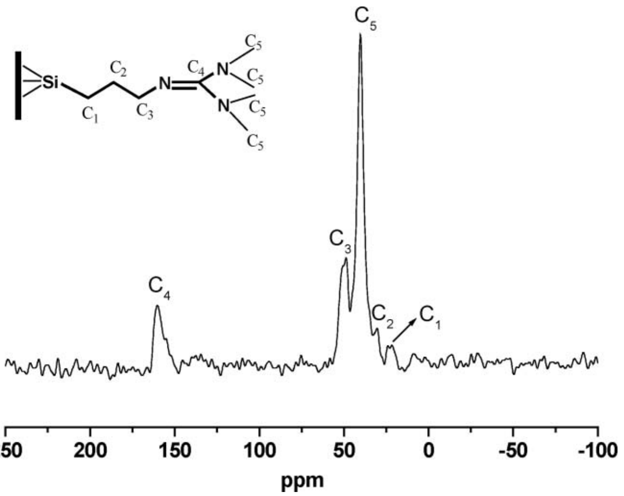


Fig. 5 ^{13}C CP-MAS NMR spectrum of G-Pd/SBA-16-G.

In order to get an insight into the coordination state of the Pd complex on the solid catalyst, UV-vis and X-ray photoelectron spectroscopy (XPS) experiments were performed. The UV-vis spectra for the Pd-G complex in solution and Pd-G/SBA-16-G are displayed in Fig. 6. In order to elucidate the coordination state of the complex in solution and on the solid surface, G in solution and SBA-16-G (G grafted on SAB-16) as references are also included in Fig. 6A and Fig. 6B, respectively. As shown in Fig. 6A, the Pd-G complex in dichloromethane exhibits two new absorption bands around 370 and 445 nm compared with G in dichloromethane. These two bands, attributable to the ligand to metal charge transfer transitions (LMCT), may be characteristics of the Pd-G complex. In Fig. 6B, Pd-G/SBA-16-G also shows two new absorption bands in comparison with the only G grafted on SBA-16 (SBA-16-G), indicating that there is a coordination interaction between PdCl$_2$ and G on the solid catalyst surface. A further comparison of the UV-vis spectra of Pd-G/SBA-16-G (Fig. 6B) and that of Pd-G complex in solution (Fig. 6A) shows that they have similar absorption bands in the range of 350–700 nm. The similar absorption bands may suggest that Pd exist on the solid catalyst surface in a coordinated fashion, which is similar to the Pd-G complex in solution.

Fig. 7 presents the XPS elemental survey scans of surface of the solid catalyst. The peaks corresponding to silicon, oxygen, carbon, nitrogen, palladium and chlorine are clearly observed. Fig. 8 displays the Pd binding energy of PdCl$_2$ and Pd-G/SBA-16-G. PdCl$_2$ exhibits two peaks centered at 342.6 and 337.3

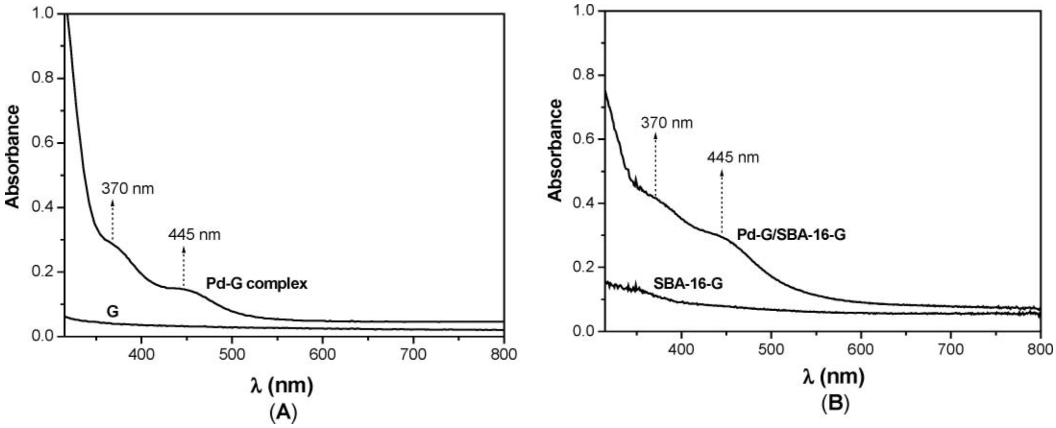


Fig. 6 UV-vis spectra. (A): Pd-G complex and G in dichloromethane; (B) Pd-G/SBA-16-G and SBA-16-G (diffuse reflectance).

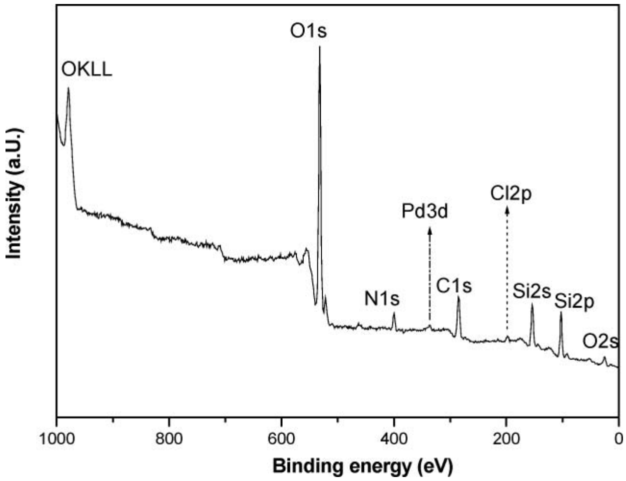


Fig. 7 XPS spectrum of the elemental survey scan of G-Pd/SBA-16-G.

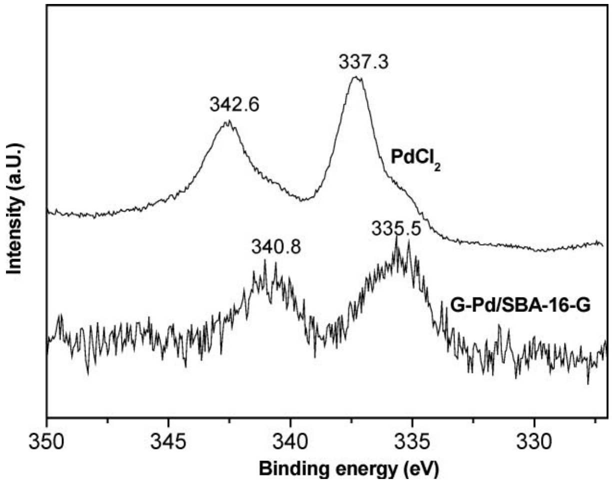


Fig. 8 XPS spectra of G-Pd/SBA-16-G and $PdCl_2$.

eV, which are assigned to Pd $3d_{3/2}$ and Pd $3d_{5/2}$, respectively. Compared with $PdCl_2$, the Pd $3d_{3/2}$ and Pd $3d_{5/2}$ peaks for Pd-G/SBA-16-G significantly shift to 340.8 and 335.5 eV, respectively. The remarkable decrease in Pd binding energy implies that there is a strong coordination interaction between Pd and G. These results are in agreement with the UV-vis observations.

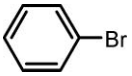
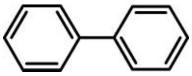
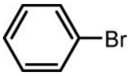
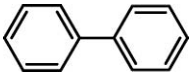
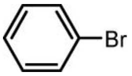
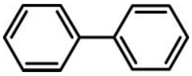
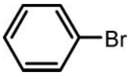
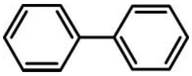
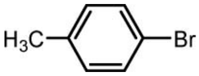
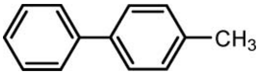
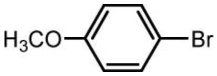
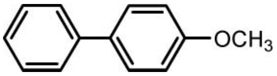
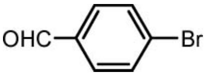
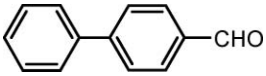
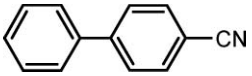
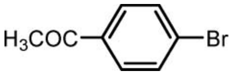
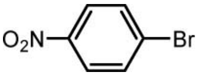
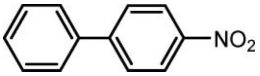
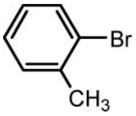
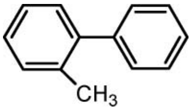
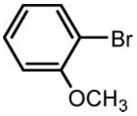
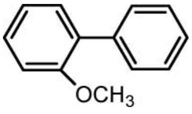
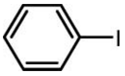
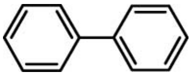
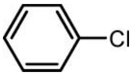
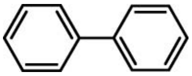
The above characterization experiments confirm that the Pd-G complex and G were successfully immobilized onto SBA-16 through a covalent linkage, the catalyst Pd-G/SBA-16-G still maintains its unique pore structure of the parent material SBA-16, and the Pd-G complex immobilized on the solid catalyst surface has a coordination state similar to the Pd-G complex in solution.

The Suzuki reaction

The catalytic activity of Pd-G/SBA-16-G was first tested using Suzuki coupling. Previous studies have showed that solvents and base had remarkable influences on the reactivity of the Suzuki reaction.[7,8] We are interested in using water as a medium for the Suzuki coupling because using water as solvent represents a green, safe and cost-effective process. Our preliminary screening of solvent reveals that the presence of ethanol could efficiently promote the Suzuki reaction in water and 50% aqueous ethanol was the best choice for the reaction medium.[4a,7,9] After the reaction medium was chosen, we screened a range of representative bases. ESI, Table S2† lists the results of the Suzuki coupling of bromobenzene and phenylboronic acid in the presence of various bases. As shown in Table S2,† under the same conditions, NaOAc afforded a low conversion. KF, $KHCO_3$ and $NaHCO_3$ gave moderate conversions. K_3PO_4 and K_2CO_3, Na_2CO_3 and other hydroxide bases afforded good to excellent conversions. Among the bases investigated, K_3PO_4 was found to be the best choice in view of the highest conversion.

With the optimized solvent and base in hand, we investigated the activity of Pd-G/SBA-16-G for various substrates. All the reactions were carried out at 50 °C in air using a 50% aqueous ethanol solution as a reaction medium. The corresponding results are summarized in Table 1. Using bromobenzene and phenylboronic acid as reactants, Pd-G/SBA-16-G at a loading of 0.1 mol% Pd (with respect to bromobenzene) afforded biphenyl in 95% yield within 20 min and a TOF *ca.* 2850 h^{-1} (Table 1, entry 1). Encouraged by so high an activity of the developed catalyst, we decided to explore the potential of the catalyst Pd-G/SBA-16-G at a lower loading. When the catalyst loading was decreased to 0.01 mol%, within 35 min

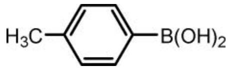
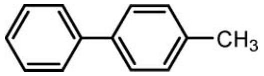
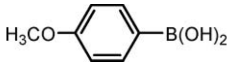
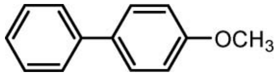
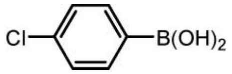
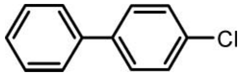
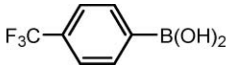
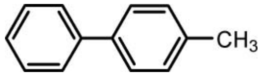
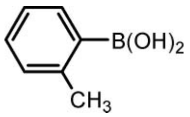
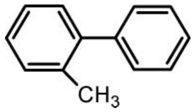
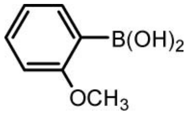
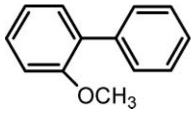
Table 1 Suzuki coupling of various bromides with phenylboronic acid in the presence of the catalyst Pd-G/SBA-16-G[a]

Entry	Substrate	Product	Pd/mol%	t/min	Yield[b] (%)	TOF[c]/h^{-1}
1			0.1	20	95	2850
2			0.01	35	99	17 000
3			0.002	100	99	29 700
4			0.001	130	99	45 700
5			0.01	50	99	11 880
6			0.01	40	79	11 850
7			0.01	35	99	16 970
8			0.01	40	97	14 550
9			0.01	50	98	11 760
10			0.01	60	93	9300
11			0.01	90	94	6270
12			0.01	100	93	5580
13			0.01	35	88	15 085
14			0.1	180	8	—

[a] The reaction was carried out at 50 °C in air. [b] Isolated yield. [c] TOF is calculated according to the following equation: TOF = $N_{\text{product}}/(N_{\text{palladium}} \times t)$, where N denotes molar numbers, and t denotes reaction time (h).

Pd-G/SBA-16-G still gave biphenyl in 99% yield and TOF reached 17 000 h^{-1} (Table 1, entry 2). The activity of the developed solid catalyst is nearly comparable to its homogeneous counterpart (Pd-tetramethylguanidine complex, 97% yield within 20 min). Further reducing the catalyst loading down to 0.002 mol%, 99% yield was achieved within 100 min and TOF was up to 29 700 h^{-1} (Table 1, entry 3). When the catalyst loading was further decreased to 0.001 mol%, 99%

Table 2 Suzuki coupling of arylboronic acids with bromobenzene in the presence of the catalyst Pd-G/SBA-16-G[a]

Entry	Substrate	Product	t/min	Yield[b] (%)	TOF[c]/h^{-1}
1			35	95	16 280
2			35	84	14 400
3			120	79	3950
4			300	98	1960
5			75	99	7920
6			100	99	5940

[a] The reaction was carried out with 4 mmol of halide, 4.4 mmol of phenylboronic acid, 4.4 mmol of $K_3PO_4 \cdot 3H_2O$, 0.01 mol% Pd with respect to bromobenzene (5 mg), 4 mL of water and 4 mL of ethanol at 50 °C in air. [b] Isolated yield. [c] TOF is calculated according to the method used in Table 1.

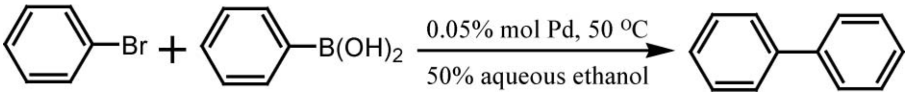
yield could be still obtained within 130 min and TOF was 45 700 h^{-1} (Table 1, entry 4). The activity of the developed catalyst is much higher than that of the *N*-heterocyclic carbene palladium complex grafted on SBA-16 (reported in our very recent study) under the same conditions.[4a] To the best of our knowledge, this finding represents one of the best cases for Suzuki coupling of bromobenzene using an immobilized catalyst under mild conditions.[10]

In order to verify the high activity of Pd-G/SBA-16-G, we examined its activity towards other substrates with variation of different substituents. These results are included in Table 1. At a catalyst loading of 0.01 mol%, Pd-G/SBA-16-G also afforded a satisfactory yield for bromides containing $-CH_3$ and $-OCH_3$ groups within 40–50 min (Table 1, entries 5 and 6). For other bromides with substituents such as –CHO, –CN, $-COCH_3$ and $-NO_2$ complete conversions were observed and 93–99% yields for the corresponding biaryl products were also achieved within one hour under mild reaction conditions (Table 1, entries 7–10). With regard to 2-substituted bromides, it took a slightly longer time to complete the reaction, probably due to steric hindrance, but TOFs still exceeded 5500 h^{-1} (Table 1, entries 11 and 12). Additionally, Pd-G/SBA-16-G showed high activity towards iodobenzene but low activity towards chlorobenzene (Table 1, entries 13 and 14).

Pd-G/SBA-16-G also showed a high activity for the Suzuki couplings of other arylboronic acids with different substituents. The results are listed in Table 2. For *p*-methylphenylboronic acid and *p*-methoxyphenylboronic acid, satisfactory yields could be obtained within 35 min (Table 2, entries 1 and 2). For arylphenylboronic acid with electron-withdrawing groups such as –Cl and $-CF_3$, good yields were still afforded although a longer time was required to complete the reaction (Table 2, entries 3 and 4). When these substituents changed to the *o*-position, a longer time was needed to achieve excellent yields compared with *p*-substituted phenylboronic acids (Table 2, entries 5 and 6). The prolonged reaction time may reflect the steric hindrance effects.

The recyclability of Pd-G/SBA-16-G was investigated with consecutive Suzuki coupling reactions. Due to the unavoidable loss of solid catalyst during the course of recovery and washing, the reaction scale was amplified 5 times to ensure catalyst quality to perform the several consecutive recycling reactions, as described in the Experimental. The recycling results of the catalyst Pd-G/SBA-16-G are summarized in Table 3. The catalyst Pd-G/SBA-16-G gave complete conversion of bromobenzene, and 99% yield was still achieved within 35 min under the scale-up conditions. The determined palladium content in the product from the first reaction cycle was below 0.1 ppm. After the first reaction cycle, the catalyst could be recovered by simple centrifugation and filtration. After being washed and dried, the recovered catalyst was directly used for the next reaction cycle. For the second reaction cycle, biphenyl in 99% yield was still obtained within 40 min. From the second to sixth reaction cycle, 84–91% yield were achieved although a longer reaction time was needed to complete the reaction. For the seventh reaction cycle, 77% yield could be attained within 15 h. Although the activity of Pd-G/SBA-16-G was decreased during the consecutive recycling reactions, it still represents one of

Table 3 Recyclability test of the catalyst Pd-G/SBA-16-G in the Suzuki reaction[a]



Cycle	1	2	3	4	5	6	7
t	35 min	40 min	100 mim	3 h	5.5 h	12 h	15 h
Yield (%)	99	99	97	87	84	91	77

[a] The fist reaction cycle was carried out with 40 mmol of halide, 44 mmol of phenylboronic acid, 44 mmol of $K_3PO_4{\cdot}3H_2O$, 0.05 mol% Pd with respect to bromobenzene (246 mg), 40 mL of water and 40 mL of ethanol at 50 °C in air. For the following reaction cycles, the recovered catalyst was weighed again and the fresh solvent and substrates was added, but the molar ratios of substrates and solvent to Pd remained the same to the first run.

the most durable catalysts in view of the low catalyst loading (0.05 mol%) employed in the recycling test. The loss in activity is mainly due to the collapse of pore structure, which leads to the inability to limiting the growth of Pd nanoparticles into less active larger particles.

The aerobic oxidation of alcohols

Selective oxidation of alcohols to carbonyl compounds is one of the most important transformations in the synthesis of fine chemicals. Currently, of particular interest in this field is the use of molecular oxygen as oxidant because it represents a green and facile chemical process in contrast to the use of toxic and expensive stoichiometric metal oxidants.[11] Encouraged by the obtained results in the Suzuki reaction, we attempted to examine the catalytic performances of Pd-G/SBA-16-G in the aerobic oxidation of alcohols.

Selected examples are listed in Table 4. The oxidation reactions were conducted in toluene under air or O_2 atmosphere using K_2CO_3 as a base. The catalyst Pd-G/SBA-16-G shows moderate activity in the oxidation of benzyl alcohol in air. Within 8 h, 48.5% conversion for benzyl alcohol was obtained at 80 °C and the selectivity for benzaldehyde was more than 99% (Table 4, entry 1). When the reaction was carried out in an O_2 atmosphere, which was introduced by using an O_2 balloon under an atmospheric pressure, complete conversion of benzyl alcohol was achieved within 8 h (Table 4, entry 2). No by-products (*e.g.* carboxylic acid) were observed. When the reaction temperature was increased to 100 °C, the reaction proceeded faster, and nearly complete conversion of benzyl alcohol was observed within a shorter time (Table 4, entry 3). The catalyst Pd-G/SBA-16-G also showed good activity towards the oxidation of other benzyl alcohol containing substituents such as methyl, methoxy and nitro groups (Table 4, entries 4–6). Carboxylic acids were not detected for all these substrates investigated. Interestingly, the catalyst Pd-G/SBA-16-G is also active for the oxidation of less reactive α, β-unsaturated alcohols like cinnamyl alcohol. 93.9% conversion and more than 99% selectivity could be obtained at the catalyst loading of 1 mol% (Table 4, entry 7). For secondary and heterocyclic alcohols, the catalyst Pd-G/SBA-16-G also shows satisfactory activity (Table 4, entries 8 and 9).

Further experiments were performed to verify the catalyst recyclability. The results of the recycling tests of the oxidation of benzyl alcohol are displayed in Fig. 9. After the first reaction cycle, the catalyst Pd-G/SBA-16-G was recovered by a simple filtration, washed with toluene and acetone, and eventually dried for the next cycle. For the second reaction cycle, Pd-G/SBA-16-G still furnished a complete conversion and over 99% selectivity within the same reaction time as the first reaction cycle (8 h). From the third to seventh reaction cycle, over 99% conversion was achieved without any prolonged time and 99% selectivity was maintained. For the eighth cycle reaction, although the activity of the reused catalyst began to decrease, 97% conversion was still obtained within 8 h. From the ninth to fourteenth reaction cycle, above 93% conversions were still afforded within a slightly prolonged time (11–13.5 h). For the fifteenth reaction cycle, 95% conversion was obtained within 14.5 h. The total TON (turnover numbers) for fifteen cycles was up to 3700. Interestingly, the selectivity for benzaldehyde was maintained over 99% throughout all the reaction cycles. These results are very encouraging in view of the previously reported results.[4g,12]

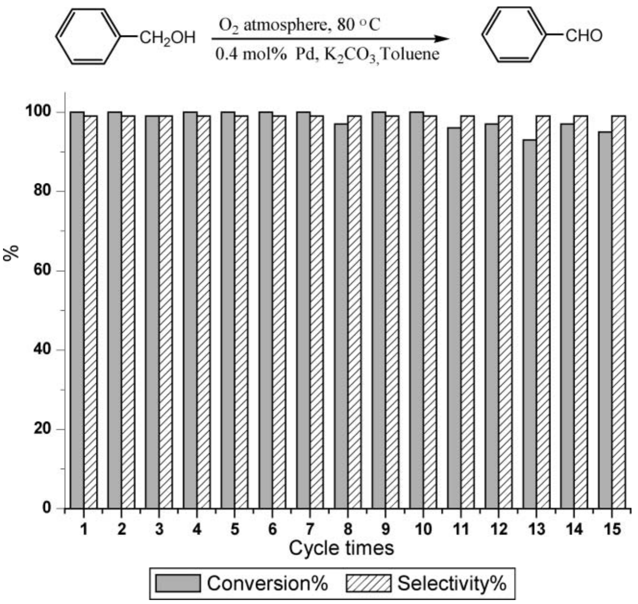
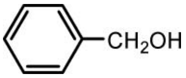
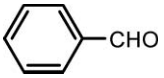
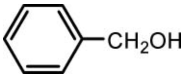
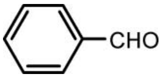
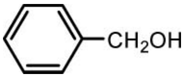
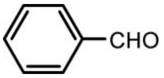
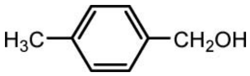
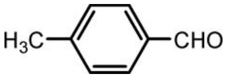
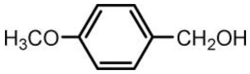
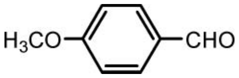
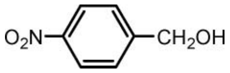
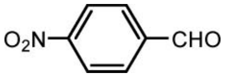
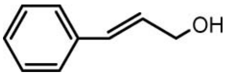
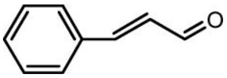
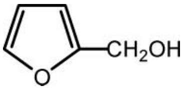
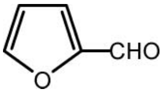
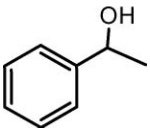
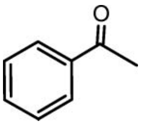


Fig. 9 Recycling test of G-Pd/SBA-16-G. The reaction time for the fist to eighth cycle was 8 h, and the reaction time for the ninth to fifteenth cycle was 11 to 14.5 h.

The impressive recyclability of the catalyst may be partially attributable to the unique pore structure of SBA-16. To confirm the role of the pore structure, TEM was employed to characterize the fresh catalyst Pd-G/SBA-16-G and the catalyst Pd-G/SBA-16-G that had been used twice. Their TEM images are shown in Fig. 10. For the fresh catalyst, Pd-G/SBA-16-G, the (100)

Table 4 The aerobic oxidation of alcohols in the presence of the catalyst Pd-G/SBA-16-G[a]

Entry	Substrates	Product	Pd mol%	T/°C	t/h	Conv. (%)	Selectivity (%)
1[b]			0.4	80	8	49	> 99
2[c]			0.4	80	8	> 99	> 99
3[c]			0.4	100	7	99	> 99
4[c]			0.4	100	6	98	> 99
5[c]			0.4	100	7	> 99	> 99
6[c]			0.4	110	20	91	> 99
7[c]			1	100	24	94	> 99
8			1	110	24	79	78
9			1	110	24	99	> 99

[a] The reactions were carried out with alcohol (2 mmol), K_2CO_3 (2 mmol), the catalyst Pd-G/SBA-16-G and toluene (2 mL) under atmospheric pressure of O_2 or air. [b] In air. [c] In an O_2 atmosphere that was introduced by an O_2 balloon under atmospheric pressure.

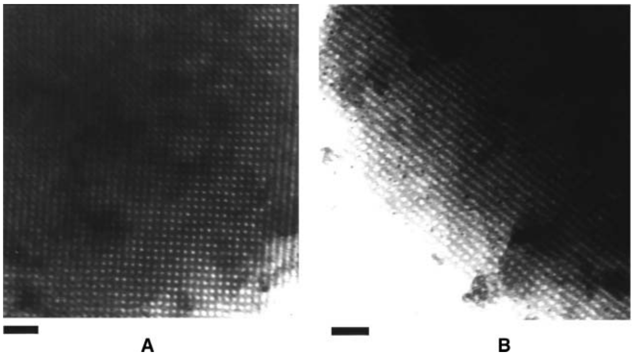


Fig. 10 TEM images for the fresh catalyst G-Pd/SBA-16-G (A) and the catalyst G-Pd/SBA-16-G used two times (B). The bar is 50 nm.

projection corresponding to a cubic *Im*3*m* structure was clearly observed (Fig. 10A). After the catalyst had been used twice, the cage-like structure of the catalyst was still observed and fine Pd particles appeared (Fig. 10B). Interestingly, the Pd particles with sizes of only a few nanometres were dispersed in the cages of SBA-16. This observation is in agreement with the previous reports that Pd nanoparticle was formed once the catalytic reaction started.[3g] Due to the high surface area and surface energy, the unstable nanoparticles are prone to aggregation and agglomeration into larger particles. Owing to the spatial restriction of the isolated nanocages and smaller pore entrances of SBA-16, the growth of Pd nanoparticles is efficiently prevented, as shown in Scheme 1. The Pd nanoparticles stabilized by the nanocages of SBA-16 may account for the high recyclability.

Conclusions

By grafting a mixture of a palladium-guanidine complex and guanidine on SBA-16 *via* a one-pot silylation, a new solid catalyst for the Suzuki coupling reaction and the aerobic oxidation of benzyl alcohols was successfully prepared. This catalyst can afford complete conversions of various aryl bromides and arylboronic acids in an aqueous ethanol solution at 50 °C even at catalyst loadings of 0.01~0.001 mol%, and the TOF for the Suzuki coupling of bromobenzene and phenylboronic acid is up to 45 700 h^{-1} under mild conditions in air. The developed solid catalyst combined with the mild conditions represents one of the most efficient heterogeneous systems for the Suzuki reaction of aryl bromides. Furthermore, it was found that the catalyst could work well for the aerobic oxidation of benzylic alcohols and cinnamyl alcohol under an atmospheric pressure of O_2, affording over 99% of selectivity. This catalyst could be reused 15 times without a significant decrease in activity and selectivity.

Experimental

Reagents and materials

Pluronic P123 copolymer ($EO_{20}PO_{70}EO_{20}$), Pluronic copolymer F127 ($EO_{106}PO_{70}EO_{106}$) and $PdCl_2$ were purchased from Sigma Company. Various arylboronic acids were obtained from Beijing Pure Chemical Co. Ltd. (3-Chloropropyl)trimethoxysilane was purchased from Jianghan Fine Chemical Company (China, distilled). 1,1,3,3-Tetramethylguanidine, aryl bromides and most of other reagents were obtained from Shanghai Chemical Reagent Company of Chinese Medicine Group.

Mesoporous cage-like material SBA-16 was synthesized according to a modified method.[6] A mixture of Pluronic F127 ($EO_{106}PO_{70}EO_{106}$, 7.42 g) and Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, 1.19 g) were used as the templates. After the mixed templates were completely dissolved in a solution of 300 mL of distilled water and 52.5 g of concentrated hydrochloric acid (36%), the solution was further stirred at 308 K for 4 h. 28 mL of tetraethyl orthosilicate was added dropwise to the solution. After being stirred for 40 min, the resulting suspension was transferred into autoclaves. The autoclaves were placed under static conditions at 308 K for 24 h. Afterwards the temperature of the autoclaves was raised up to 373 K and kept at that temperature for 32 h. After the hydrothermal treatment, the precipitated solid was isolated by filtration and dried at 373 K for 24 h, yielding white solid powders. This powdered sample was then subjected to calcination at 825 K for 10 h and the mesoporous cage-like material SBA-16 was eventually obtained.

Preparation of 1,1,3,3-tetramethyl-2-(3-trimethoxysilylpropyl)-guanidine (G)[13]

In a dry flask, 1,1,3,3-tetramethylguanidine (17.39 g, 0.151 mol) and xylene (1.8 mL) were mixed together. After being evacuated and purged with N_2 five times, the system was heated up to 120 °C and maintained at this temperature for 2 h, and then (3-chloropropyl)trimethoxysilane (14.93 g, 0.076 mol) was added dropwise over 2 h. After being stirred at 120 °C for 7 h under an N_2 atmosphere, the resulting mixture was allowed to cool down to room temperature. The formed salt precipitates 1,1,3,3-tetramethylguanidine·HCl was filtrated out. The filtrate liquid was distilled under reduced pressure and 1,1,3,3-tetramethyl-2-(3- trimethoxysilylpropyl)-guanidine was thus obtained (yield: *ca.*18%). 1,1,3,3-tetramethyl-2-(3-trimethoxysilylpropyl)-guanidine was denoted as G hereafter. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 0.63 (m, 2 H, $SiCH_2$); 1.57 (m, 2 H, $SiCH_2CH_2$); 2.58–2,73 (m, 12 H, NCH_3); 3.05 (m, 2 H, $CH_2N{=}C$); 3.55 (s, 9 H, CH_3O). ^{13}C NMR ($CDCl_3$, 300 MHz, ppm): δ 6.55 ($SiCH_2$); 24.78 ($SiCH_2CH_2$); 39.75 (NCH_3); 50.5 (CH_3O, $CH_2N{=}C$); 160.65 ($N{=}C(N(CH_3)_2)_2$.

Preparation of a G solution containing Pd-G complex (Pd-G)

In a dried flask, $PdCl_2$ (0.032 g) was added to 1,1,3,3-tetramethyl-2-(3- trimethoxysilylpropyl)-guanidine (G, 0.5 g). The system was evacuated and purged four times with N_2. The mixture was stirred at 55 °C for 12 h and was then cooled to room temperature, affording a red liquid, which was named as G solution containing the Pd-G complex.

One-pot immobilization of Pd-G complex and G on SBA-16

The above G solution containing the Pd-G complex was diluted with 10 mL of dry toluene. Into this solution, 1.6 g of SBA-16 was added under a N_2 atmosphere and the mixture was stirred at 80 °C for 8 h. On cooling, the solid material was isolated by filtration, and repeatedly washed with toluene, dichloromethane and acetone in sequence, and then dried under vacuum overnight to give the yellowish solid catalyst Pd-G/SBA-16-G. The Pd content of Pd-G/SBA-16-G determined by ICP-AES is 0.86 wt%. The N and C contents of Pd-G/SBA-16-G determined by combustion chemical analysis are 3.58 wt% and 9.28 wt%, respectively.

Typical procedures for the Suzuki reaction

A mixture of bromobenzene (8 mmol), phenylboronic acid (8.8 mmol), $K_3PO_4\cdot 3H_2O$ (8.8 mmol), ethanol (8 mL), H_2O (8 mL), and Pd-G/SBA-16-G (9.86 mg) were stirred at 50 °C in air. The reaction process was monitored by TLC. After the reaction, the mixture was cooled down to room temperature and repeatedly extracted with diethyl ether (8×8 mL). The combined organic layers were concentrated and the resulting product was purified by column chromatography on silica gel. The product was confirmed by ^{1}H NMR.

Recyclability tests for the Suzuki reaction were as follows: for the first run, the mixture of 40 mmol of bromobenzene, 44 mmol of phenylboronic acid, 44 mmol of $K_3PO_4\cdot 3H_2O$, 0.05 mol% Pd with respect to bromobenzene (246 mg), 40 mL of water and 40 mL ethanol were stirred at 50 °C. The reaction was monitored by TLC. At the end of the reaction the system was cooled down to room temperature and repeatedly extracted with diethyl ether. The obtained catalyst was washed with diethyl ether, water, methanol and acetone in sequence and dried under vacuum. The recovered catalyst was weighed again. Fresh solvent and substrates were added, but the molar ratios of substrates and solvent to Pd remained the same to the first run.

Typical procedures for the oxidation of benzyl alcohol by O_2

Benzyl alcohol (2 mmol), K_2CO_3 (2 mmol), the catalyst Pd-G/SBA-16-G (0.4 mol% equiv. to benzyl alcohol, 98.6 mg) and toluene (2 mL) were combined in a dry flask, and the mixture was stirred at a given temperature in air or O_2 for a given time. Oxygen gas was introduced into the flask from an O_2 balloon under atmospheric pressure. After the reaction, the liquid obtained by filtration was diluted with toluene and then analyzed with GC to determine the conversion and selectivity.

Recyclability tests for the oxidation of benzyl alcohol were as follows: for the first cycle, the procedure was the same to the above description. After the first cycle reaction, the solid catalyst was recovered by centrifugation, and washed repeatedly with dry toluene and acetone. The recovered catalyst was dried under vacuum and was directly used for the next cycle reaction. For each cycle reaction, 0.2 mmol of K_2CO_3 (10% equiv. to the first reaction cycle) was supplied into the reaction system.

Characterization and analysis

Small-angle powder X-ray powder diffraction was performed on a Rigaku diffractometer (Cu Kα, 40 kV, 30 mA). N_2 physical adsorption was carried out on Micromeritics ASAP2020 volumetric adsorption analyzer (before the measurements, samples were out gassed at 393 K for 6 h). The Brunauer–Emmett–Teller (BET) surface area was evaluated from the data in the relative pressure range of 0.05 to 0.25. The total pore volume of each sample was estimated from the amount adsorbed at the highest P/P_0 (above 0.99). Pore diameters were determined from the adsorption branch using the Barrett–Joyner–Halenda (BJH) method. FT-IR spectra were collected on Thermo-Nicolet-Nexus 470 infrared spectrometer. UV-vis spectra were recorded on the JASCOV-550 UV-vis spectrophotometer. Diffuse-reflectance UV-vis spectra were also recorded on the CARY300 spectrophotometer (Varian Co.). Pd content was analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES, AtomScan16, TJA Co.). C and N content analysis was conducted on a vario EL (Elementar). X-Ray photoelectron spectroscopy (XPS) was recorded on Perkin-Elmer 5400 ESCA, and C_{1s} line at 284.9 eV was used as a reference. TEM micrographs were taken with a JEM-2000EX transmission electron microscope at 120 kV. Solid-state NMR spectra were recorded on an Infinityplus 300 MHz spectrometer: for ^{13}C CP-MAS NMR experiments, 75.4 MHz resonant frequency, 4 kHz spin rate, 4 s pulse delay, 1.0 ms contact time, hexamethyl benzene as a reference compound; for ^{13}Si MAS NMR experiments, 79.6 MHz resonant frequency, 4 kHz spin rate, 4.0 s pulse delay, TMS as a reference compound. GC analysis was conducted on SP-6800A equipped with SE-54 capillary column.

The ^{1}H NMR data for the coupling products

Biphenyl ($CDCl_3$, 300 MHz, ppm): δ 7.57 (d, 4 H, J = 9 Hz); 7.41–7.46 (m, 4 H); 7.34 (t, 2 H, J = 7.5 Hz). 4-Biphenylcarbaldehyde ($CDCl_3$, 300 MHz, ppm): δ 10.07 (s, 1 H); 7.95 (d, 2 H, J = 7.8 Hz); 7.75 (d, 2 H, J = 7.8 Hz), 7.43–7.66 (m, 5 H). 4-Acetylbiphenyl ($CDCl_3$, 300 MHz, ppm): δ 8.06 (d, 2 H, J = 6 Hz); 7.39–7.68 (m, 7 H); 2.67 (s, 3 H). 4-Cyanobiphenyl ($CDCl_3$, 300 MHz, ppm): δ 7.53–7.64 (m, 4 H); 7.50 (d, 2 H, J = 7.8 Hz); 7.35–7.42 (m, 3 H). 4-Nitrobiphenyl ($CDCl_3$, 300 MHz, ppm): δ 8.29 (d, 2 H, J = 8.7 Hz); 7.73 (d, 2 H, J = 8.7 Hz); 7.45–7.62 (m, 5 H). 4-Methylbiphenyl ($CDCl_3$, 300 MHz, ppm): δ 7.52 (d, 2 H, 6 Hz); 7.43 (d, 2 H, 6 Hz); 7.37 (t, 2 H, 6 Hz); 7.27 (d, 1 H, 6 Hz); 7.21 (d, 2 H, 9 Hz); 2.34 (s, 3 H). 4-Methoxybiphenyl ($CDCl_3$, 300 MHz, ppm): δ 7.55–7.60 (m, 4 H); 7.45 (t, 2 H, J = 7.5 Hz); 7.33 (m, 1 H); 7.00 (d, 2 H, J = 9 Hz); 3.88 (s, 3 H). 2-Methoxybiphenyl ($CDCl_3$, 300 MHz, ppm): δ 7.48–7.51 (m, 2 H); 7.19–7.36 (m, 5 H); 6.86–6.98 (m, 2 H); 3.66 (s, 3 H). 2-Methoxybiphenyl ($CDCl_3$, 300 MHz, ppm): δ 7.09–7.24 (m, 9 H); 2.14 (s, 3 H). 4-Trifluoromethylbiphenyl ($CDCl_3$, 300 MHz, ppm): δ 7.67 (s, 4 H), 7.57–7.59 (d, J = 6.9 Hz, 2 H), 7.38–7.48 (m, 3 H). 4-Chlorobiphenyl ($CDCl_3$, 300 MHz, ppm): δ 7.53–7.56 (m, 4 H), 7.35–7.50 (m, 5 H).

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