N-Heterocyclic carbene palladium complex supported on ionic liquid-modified SBA-16: an efficient and highly recyclable catalyst for the Suzuki and Heck reactions

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By grafting an *N*-heterocyclic carbene palladium complex and ionic liquid on the mesoporous cage-like material SBA-16, an efficient and highly recyclable heterogeneous catalyst for the Suzuki and Heck reactions was prepared. This catalyst afforded a fast conversion of the unactivated bromobenzene at a catalyst loading of 0.01 mol%, and a good yield was still achieved after the catalyst was reused ten times. Its recyclability was much better than that of the catalyst prepared from amorphous silica. The significantly enhanced recyclability could be attributed to the isolated nanocages of SBA-16 which could efficiently prevent the aggregation and agglomeration of Pd particles formed during the catalytic reaction into the less active large particles. The strategy for stabilizing metal nanoparticles using the isolated nanocages may be applied to other catalytic systems, in which the aggregation of metal nanoparticles is desired to be prevented.

Introduction

The Pd-catalyzed Heck and Suzuki reactions are well-known as important methods to construct C–C bond in modern chemical transformations because of the usefulness and wide applicability to various substrates.[1] Homogeneous catalysts for the reactions such as phosphine, *N*-heterocyclic carbene and palladacyclic complexes have been successfully established.[2] These homogeneous catalysts, however, suffer from the practical problems such as catalyst separation, catalyst recycling and product contamination. To address these problems, palladium complexes or nanoparticles were immobilized on various supports such as silica, alumina, zeolite, organic polymers and dendrimers to create heterogeneous catalysts because of the easy handling, recyclability and "green" process of the heterogeneous systems.[3] The extensive explorations of heterogeneous catalytic systems are evidenced by a great number of publications and reviews in recent years. However, heterogeneous catalysts with excellent recyclability, which is the key factor for the practical applications, are still limited.

One of the major reasons for poor recyclability is the aggregation and agglomeration of Pd naonoparticles into less active large particles (even bulk Pd) during the reaction due to the high surface energy of nanoparticles. Even for these systems using molecular catalysts, the aggregation and agglomeration still occurred because Pd nanoclusters were formed as the reaction proceeded.[4] The aggregation and agglomeration of Pd nanoclusters lead to the drastic decrease in activity of the reused catalysts. The recyclability of the heterogeneous catalysts is thus discounted.[5]

Our previous investigation and other groups' work revealed that support structure and functional groups grafted on the support played an important role in preventing the aggregation of palladium nanoparticles into the less active large particles.[6] Among various supports for immobilizing palladium catalysts, the mesoporous materials are very promising because of their high surface area and regularly arranged pore structure. Different to the mesoporous materials MCM-41 and SBA-15 which are widely used as supports, the recently synthesized SBA-16 (cubic, *Im3m*) is one of new ordered mesoporous materials with cage-like structures.[7] This mesoporous cage-like material has tunable cage size (4–10 nm) and tunable pore entrance size (generally less than 4 nm). The isolated nanocages are three-dimensionally interconnected by pore entrances. Such a nanocage of SBA-16 can not only accommodate metal particles but also, in principle, limit the growth of metal particles by the spatial restrictions. The smaller pore entrances may inhibit the motion of metal nanoparticles, thereby preventing the undesired aggregation and agglomeration. At the same time, the ionic liquids are able to be used as not only "green" reaction media but also stabilizers for metallic particles due to their electrostatic interactions and the coordination with metal atoms on the surface of metal particles.[8]

In this work, the mesoporous cage-like material SBA-16 was chosen as a support and imidazolium ionic liquid was employed to modify the surface of SBA-16. An *N*-heterocyclic carbene palladium complex was used as a molecular catalyst for immobilization because of easy synthesis from the imidazolium ionic liquid.[4b] By grafting the *N*-heterocyclic carbene palladium complex and ionic liquid on the internal surface of the nanocages of SBA-16, we have successfully prepared an efficient heterogeneous catalyst for the Suzuki and Heck reactions. This catalyst

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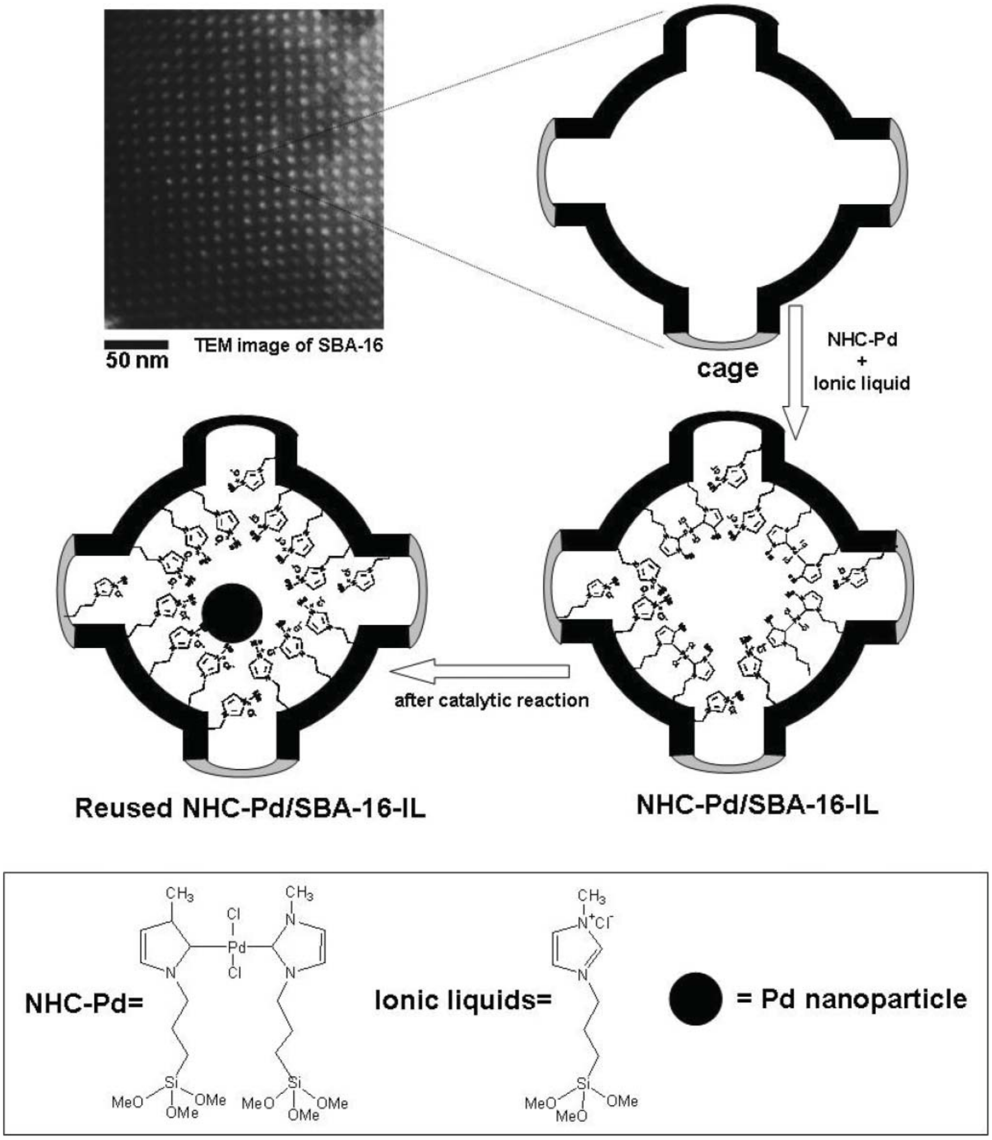


Scheme 1 Schematic descriptions for preparing the heterogeneous catalyst NHC-Pd/SBA-16-IL and the model for the reused catalyst.

afforded complete conversions of various aryl bromides even at the catalyst loading of 0.01 mol%, and could be easily recovered by a filtration. A satisfactory yield was obtained even after the catalyst was reused ten times. Furthermore, its recyclability was further highlighted by a comparison with that of the catalyst prepared from amorphous silica.

Results and discussion

Catalyst preparation and characterization

The process for the preparation of the catalyst NHC-Pd/SBA-16-IL is schematically described in Scheme 1. In order to graft the *N*-heterocyclic carbene palladium complex (NHC-Pd) and imidazolium ionic liquid (IL) on the internal surface of the cages of SBA-16, the silanols on the external surface of SBA-16 were first passivated with Ph_2SiCl_2 according to the reported method (this process is omitted in Scheme 1 for clarity).[9] To form the covalent linkage with the surface of SBA-16, the ionic liquid and NHC-Pd complex were first subjected to a derivation with a trimethoxysilyl group, as described in the Experimental. The trimethoxysilyl derivatives of NHC-Pd complex and ionic liquid were then grafted on the internal surface of SBA-16 with passivation through a one step silylation, eventually yielding the catalyst NHC-Pd/SBA-16-IL.

The process for preparing the catalyst was monitored by N_2 sorption. The N_2 sorption isotherms and pore size distribution of the corresponding samples are displayed in Fig. 1 and Fig. 2, respectively. The textural parameters determined by N_2 sorption are listed in Table 1. SBA-16 exhibited a type-IV isotherm pattern with an H2 hysteresis loop, which is characteristic of the mesoporous cage-like structure. Similar to the parent SBA-16, SBA-16 passivated with Ph_2SiCl_2 also showed a type-IV isotherm with an H2 hysteresis loop, indicating that the mesoporous cage-like structure was maintained after passivation. It is worthwhile to note that the surface area and pore volume of SBA-16 with passivation were slightly decreased. The cage size decreased by only 0.1 nm and this value is much

Table 1 Textural parameters of SBA-16, SBA-16 with passivation and NHC-Pd/SBA-16-IL

Samples	S^a/m^2 g^{-1}	V^b/cm^3 g^{-1}	Cage size^c/nm	Decrease in cage size^d/nm
SBA-16	763	0.80	6.7	—
SBA-16 with passivation	604	0.68	6.6	0.1
NHC-Pd/SBA-16-IL	207	0.22	6.1	0.6

[a] BET surface area. [b] Single point pore volume calculated at relative pressure P/P_0 of 0.99. [c] BJH method from adsorption branch. [d] The decreased value of cage diameter, compared with the cage size of the parent SBA-16.

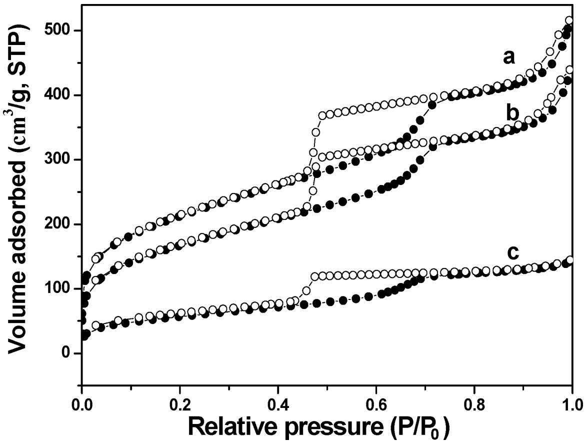


Fig. 1 N_2 sorption isotherms of samples: (a) SBA-16; (b) SBA-16 with passivation; (c) NHC-Pd/SBA-16-IL.

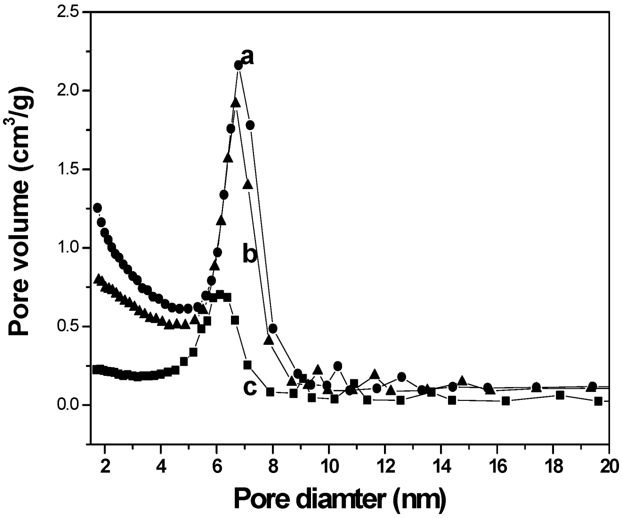


Fig. 2 Pore size distribution of samples: (a) SBA-16; (b) SBA-16 with passivation; (c) NHC-Pd/SBA-16-IL.

less than the molecular size of diphenyl silane (*ca.* 0.6 nm). This result points to the fact that the most of diphenyl silane groups were grafted on the external surface of SBA-16, as expected; otherwise the decrease in cage size should be much larger than 0.1 nm. After further grafting of the NHC-Pd complex and ionic liquid, the surface area and pore volume showed a significant decrease, and the cage size decreased again by 0.5 nm, suggesting that the NHC-Pd complex and ionic liquid were introduced into the interior of SBA-16. However, the mesoporous cage-like structure for NHC-Pd/SBA-16-IL was still maintained, as evidenced by its type-IV isotherm with an H2 hysteresis loop. The ordered mesoporous structure of NHC-Pd/SBA-16-IL was further confirmed by the XRD pattern similar to that of the parent material SBA-16 (in Fig. 3).

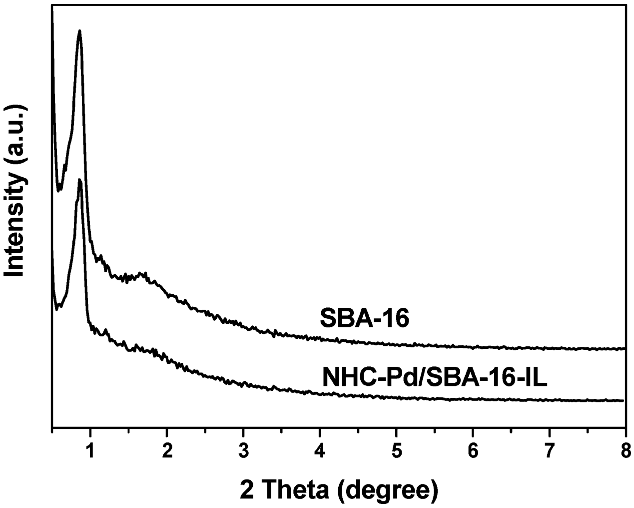


Fig. 3 XRD patterns of SBA-16 and NHC-Pd/SBA-16-IL.

NHC-Pd/SBA-16-IL was further characterized with FT-IR spectroscopy (Fig. 4) and solid state NMR (Fig. 5 and Fig. 6). In Fig. 4, the FT-IR spectroscopy of NHC-Pd/SBA-16-IL exhibited three new peaks around 1580, 2972 and 3078 cm^{-1}, compared with the FT-IR spectroscopy of SBA-16. These three peaks corresponded to the ring vibration of the imidazole, the stretching vibration of saturated C–H and the stretching vibration of unsaturated C–H on the imidazole ring, respectively. In Fig. 5, the carbon chemical shifts of the imidzaolium ionic liquid measured by ^{13}C CP-MAS NMR were in good agreement with the theoretically predicted values. As displayed in Fig. 6, the ^{29}Si MAS NMR spectroscopy of NHC-Pd/SBA-16-IL showed a "T^3" band at *ca.* −66 ppm, indicating that trimethoxysilyl derivatives of imidzaolium ionic liquid and NHC-Pd complex were immobilized on the SBA-16 through a condensation

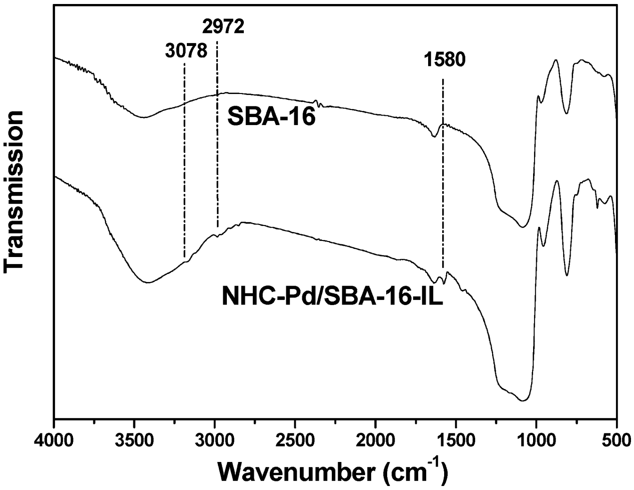


Fig. 4 FT-IR spectra of SBA-16 and NHC-Pd/SBA-16-IL.

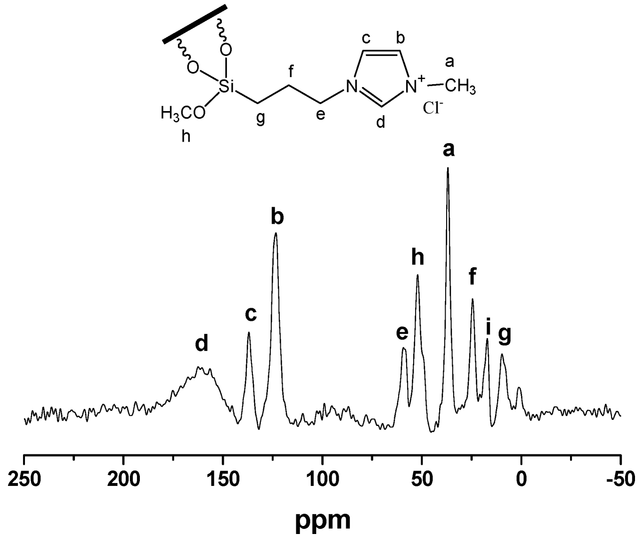


Fig. 5 ^{13}C CP-MAS NMR spectroscopy of NHC-Pd/SBA-16-IL. a, b, c, d, e, f, g, h denote the carbon atoms and the corresponding peaks, the peak denoted by i may be attributed to the carbon atoms of CH_3COO^- in the NHC-Pd complex.

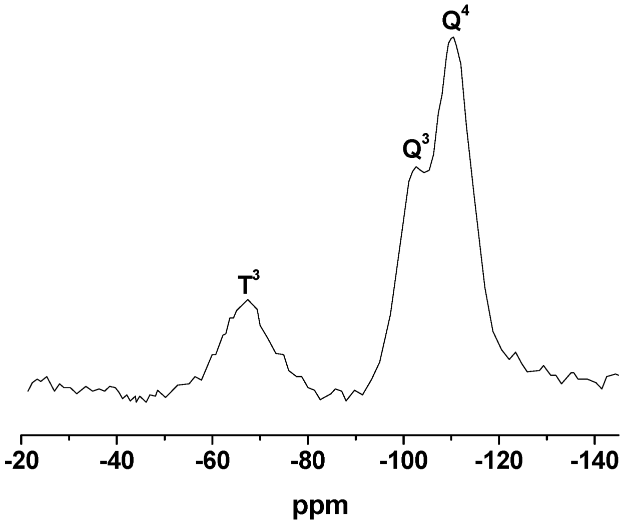


Fig. 6 ^{29}Si CP-MAS NMR spectroscopy of NHC-Pd/SBA-16-IL.

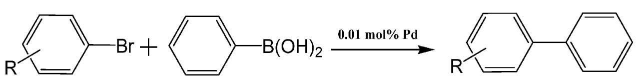
reaction of the surface silanols and trimethoxysilyl derivatives. The formation of the NHC-Pd complex was confirmed by XPS spectroscopy in view of the fact that the Pd 3d binding energy values changed form 338.7 eV to 336.5 eV after the ionic liquid was reacted with $Pd(OAc)_2$.

The above characterizations confirmed that the NHC-Pd complex and ionic liquid were successfully grafted on the surface of SBA-16.

Catalyst testing for the Suzuki reaction

The catalytic activity of NHC-Pd/SBA-16-IL was first tested in the Suzuki reaction using various aryl bromides and phenylboronic acid as substrates. All the reactions were carried out at 50 °C under air using 50% aqueous ethanol as a reaction medium. The reaction results are summarized in Table 2. NHC-Pd/SBA-16-IL was very active for the Suzuki reaction even under such mild conditions. At a catalyst loading as low as 0.01 mol%, NHC-Pd/SBA-16-IL afforded a complete conversion of bromobenzene within 5 hours, and formation of biphenyl with 99% yield (Table 2, entry 1). For the aryl bromides bearing electron-withdrawing groups, including –CHO, $–COCH_3$, $–NO_2$ and –CN, complete conversions were observed and 87–99% yields of the corresponding biaryl products could also be achieved under mild reaction conditions (Table 2, entries 2–5). For the aryl bromides bearing electron-donating groups, such as $–CH_3$ and $–OCH_3$, NHC-Pd/SBA-16-IL still showed a high activity, and 99% yield of the products were obtained within a slightly longer time (Table 2, entries 6 and 7).

Table 2 The Suzuki reaction in the presence of NHC-Pd/SBA-16-IL under air[a]



Entry	R	Reaction time/h	Isolated yield (%)
1	H	5	99
2	4-CHO	6	98
3	$4-COCH_3$	7	87
4	4-CN	7	99
5	$4-NO_2$	7	99
6	$4-CH_3$	8	99
7	$4-OCH_3$	10	99

[a] The reaction was carried out with 4 mmol of halide, 4.4 mmol of phenylboronic acid, 4.4 mmol of K_3PO_4, 0.01 mol% Pd with respect to aryl bromides, 4 mL of water and 4 mL of ethanol at 50 °C.

The recyclability of NHC-Pd/SBA-16-IL was further investigated because the recyclability of the heterogeneous catalyst is one of the most important issues for practical applications. Due to the unavoidable loss of solid catalyst during the recovery and washing, the reaction scale was amplified 8 times to ensure enough catalyst quality to perform the consecutive recycling reactions, as described in the Experimental. The recycling results of the catalyst NHC-Pd/SBA-16-IL are displayed in Fig. 7. The catalyst NHC-Pd/SBA-16-IL gave a complete conversion of bromobenzene, and 99% yield was achieved within 5 hours

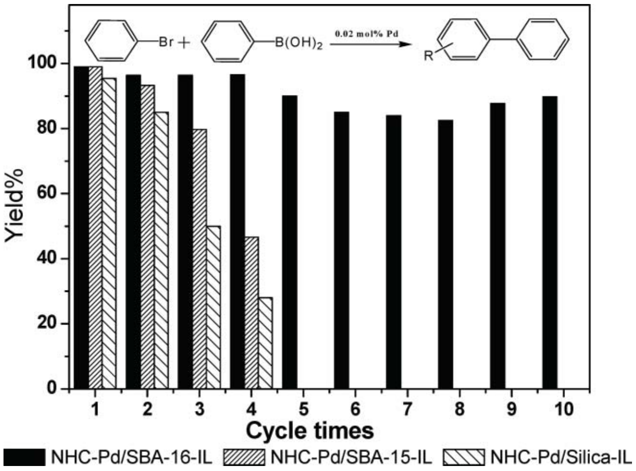


Fig. 7 The recycling testing of NHC-Pd/SBA-16-IL, NHC-Pd/SBA-15-IL and NHC-Pd/silica-IL. Reaction times from 5 to 49 h; for the recycling test, the reaction time for NHC-Pd/SBA-16-IL, NHC-Pd/SBA-15-IL and NHC-Pd/silica-IL was the same.

under the scale-up conditions. After the first reaction cycle, the catalyst NHC-Pd/SBA-16-IL could be recovered by a simple centrifugation and filtration. After being washed and dried, the recovered catalyst was directly used for the next cycle. For the second, third and fourth cycle of NHC-Pd/SBA-16-IL, 96%, 96% and 97% yield of biphenyl could still be obtained, respectively. Furthermore, a satisfactory yield was still obtained from the fifth cycle to the ninth cycle although a longer reaction time was needed to complete the reaction. 90% yield could be obtained even for the tenth cycle of NHC-Pd/SBA-16-IL within 49 hours. The total TON (turnover numbers) for ten cycles was up to 45 400. As far as we know, among the grafted catalysts, this was one of the best catalysts for the Suzuki reaction of unactivated bromobenzene in view of the high activity and excellent recyclability at the low catalyst loading (0.02 mol%).[8c–i] The high recyclability may be attributed to the mesoporous cage-like structure of SBA-16.

In order to confirm the impact of the mesoporous cage-like structure of SBA-16 on the recyclability, the NHC-Pd complex and ionic liquid were immobilized on channel-like SBA-15 and amorphous silica through the same procedures, resulting in NHC-Pd/SBA-15-IL and NHC-Pd/silica-IL, respectively. Comparative tests for the recyclability were conducted. The recycling results of NHC-Pd/SBA-15-IL and NHC-Pd/silica-IL are also included in Fig. 7. Within the same reaction time as NHC-Pd/SBA-16-IL, NHC-Pd/SBA-15-IL gave 99%, 93%, 80%, and 47% yields of biphenyl for the first, second, third and fourth cycle. NHC-Pd/silica-IL gave 95%, 85%, 50% and 25% yields. The yield for the two latter catalysts dramatically decreased upon recycling. Obviously, the recyclability of NHC-Pd/SBA-16-IL was much better than that of NHC-Pd/SBA-15-IL and NHC-Pd/silica-IL.

To further understand the underlying reason for the significant difference in recyclability, XPS and TEM were employed to characterize the fresh and reused NHC-Pd/SBA-16-IL. The XPS spectra are shown in Fig. 8. For the fresh NHC-Pd/SBA-16-IL, the Pd $3d_{5/2}$ and Pd $3d_{3/2}$ binding energies were determined to be 336.5 and 341.7 eV, respectively. These values correspond to the Pd(II) binding energy of NHC-Pd(II) complex. After being reused three times, the Pd $3d_{5/2}$ and Pd $3d_{3/2}$ binding energies changed to 334.5 and 339.9 eV, corresponding to Pd(0) binding energy. The XPS results showed that Pd(0) was formed during the catalytic reaction. This was in an agreement with the previous reported results that Pd(0) nanoparticles were evolved during the catalytic reaction, although the molecular complex was used as the initial catalyst.[4]

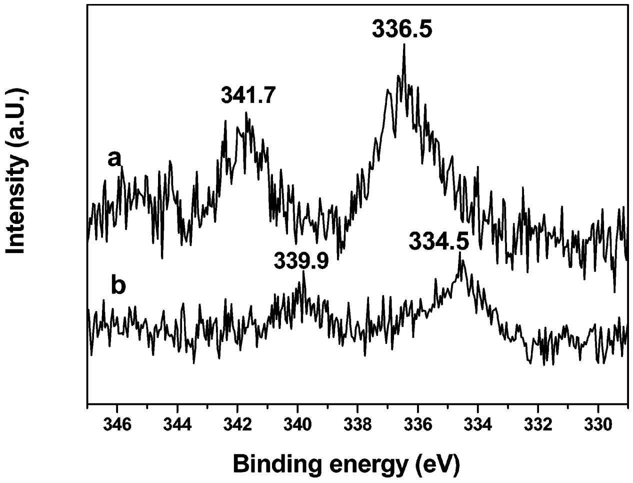


Fig. 8 XPS spectra of the fresh NHC-Pd/SBA-16-IL and the reused NHC-Pd/SBA-16-IL. a: the fresh NHC-Pd/SBA-16-IL; b: NHC-Pd/SBA-16-IL reused three times.

TEM images provided the further information about the Pd particles. TEM images for the fresh NHC-Pd/SBA-16-IL and fresh NHC-Pd/silica-IL, the NHC-Pd/SBA-16-IL reused three times and NHC-Pd/silica-IL reused three times are displayed in Fig. 9. For the fresh catalyst NHC-Pd/SBA-16-IL (Fig. 9a), the (100) projection corresponding to a cubic *Im3m* structure was clearly observed. After being reused three times, the cage-like structure of the catalyst could be still observed although the cage-like structure collapsed to some extent (Fig. 9c). Interestingly, a portion of fine Pd particles with sizes of less then 5 nm dispersed in the cages of SBA-16 were observed. However, for the catalyst NHC-Pd/silica-IL after being reused three times, it was observed that Pd particles were in the range of 10–25 nm and not uniform in size (Fig. 9d). This observation was broadly in agreement with the finding that Pd particles with sizes of 10–40 nm were formed after the catalyst derived from amorphous silica was used three times.[4b] Obviously, the sizes are much larger than the sizes of Pd particles of the NHC-Pd/SBA-16-IL reused three times. The larger Pd particles led to the drastic decrease in activity because the Pd particles of a few nanometres are active species. The size differences of Pd particles between NHC-Pd/SBA-16-IL and NHC-Pd/silica-IL accounted for their difference in recyclability.

The smaller Pd particles with a relatively uniform distribution in size may be attributed to the mesoporous cage-like structure of SBA-16. Once the catalytic reaction started, Pd(0) was formed *in situ* and then evolved into Pd nanoclusters. Due to the high surface energy, the unstable nanoclusters 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 aggregation or agglomeration of Pd clusters was efficiently prevented, as shown in Scheme 1. Accordingly, the size of Pd particles was limited to be less than the cage size of SBA-16.

Catalyst testing for the Heck reaction

Encouraged by the achievements in the Suzuki reaction, we expected to able to generalize the application of the catalyst in the Heck reaction. Table 3 summarizes the results of the Heck reaction in the presence of NHC-Pd/SBA-16-IL. Using unactivated bromobenzene and styrene as substrates, NHC-Pd/SBA-16-IL at a loading of 0.01 mol% Pd afforded a complete conversion and 94% yield was obtained (Table 3, entry 1). For bromobenzene with electron-withdrawing groups, including –$COCH_3$ and –CHO, –NO_2 and –CN, the reaction proceed relatively faster and 84%–95% yields of the corresponding products were obtained. For bromobenzene with an electron-donating group (–CH_3) the reaction proceeded slower, and 82% yield was obtained. Using substituted aryl bromides and methyl acrylate as substrates, good yields could be also obtained.

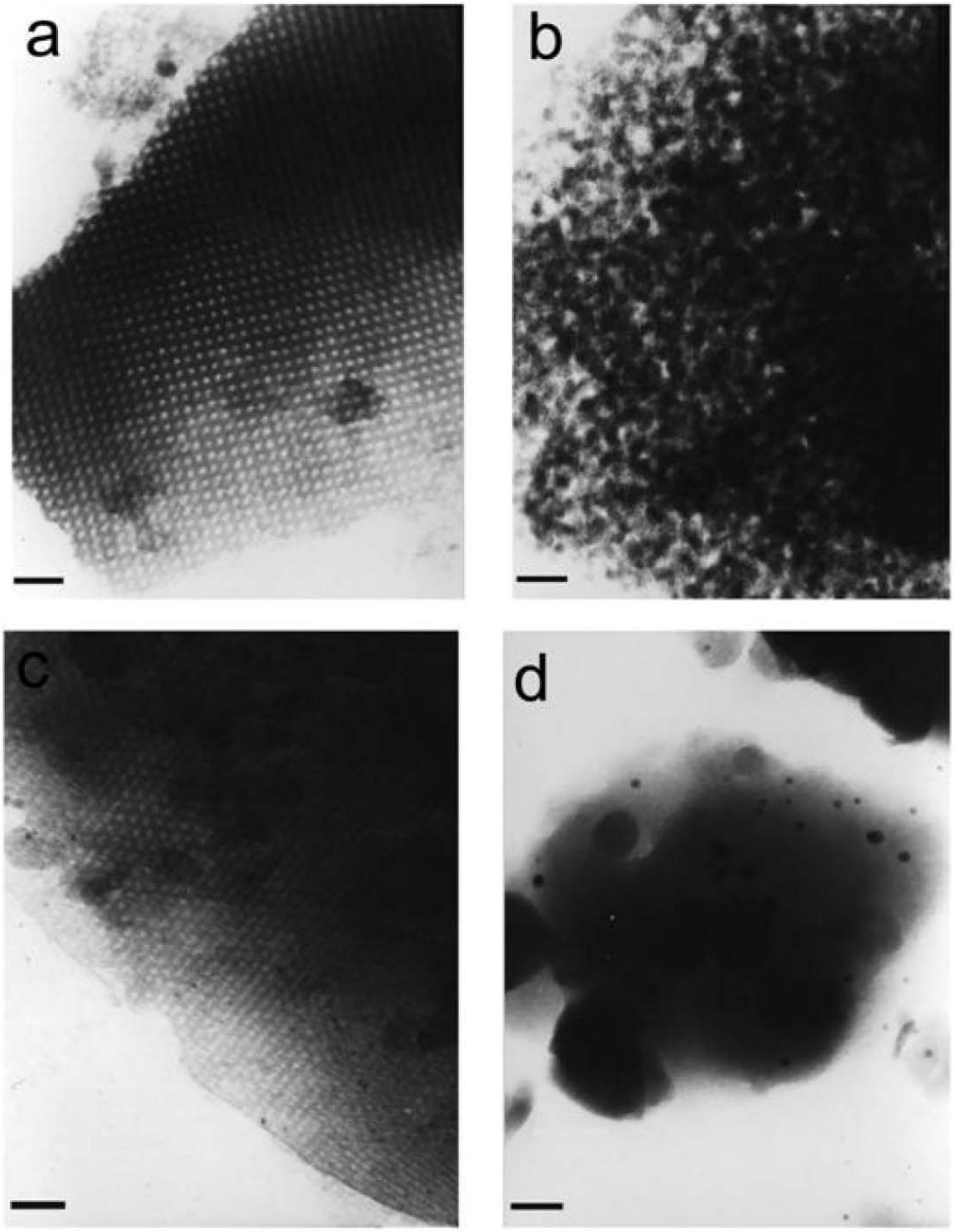
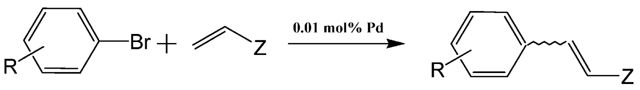


Fig. 9 TEM images for the fresh (or reused) NHC-Pd/SBA-16-IL and the fresh (or reused) NHC-Pd/silica-IL; the bar is 50 nm. a: the fresh NHC-Pd/SBA-16-IL; b: the fresh NHC-Pd/silica-IL; c: the NHC-Pd/SBA-16-IL reused three times; d: NHC-Pd/silica-IL reused three times.

To determine the heterogeneity of the reaction, the activity of the filtrate was tested. The solid catalyst was filtered out after the reaction proceeded for 5.5 h and the determined conversion was 69%. The obtained filtrate was continually stirred under the reaction conditions. After 35 hours the conversion was determined to still be 69%. This result indicated that the catalytic reaction was caused by the solid catalyst instead of leached Pd in filtrate. ICP-AES analysis of palladium content in the filtrate after the first cycle was below 0.1 ppm. The recyclability of NHC-Pd/SBA-16 was also tested with the consecutive Heck reactions. Fig. 10 displays the results of the Heck reaction between 4-bromobenzaldehyde and styrene. The first cycle of the reaction afforded 99% yield. After the first cycle reaction, NHC-Pd/SBA-16-IL was recovered by a simple filtration, successively rinsed with NMP, distilled water (to remove excess of base), ethanol and ether, and finally dried for the next cycle. Although a longer reaction time was needed to complete the reaction for the reused catalysts, a satisfactory yield (above 89%) was still obtained. 87% yield could be obtained even after the eighth cycle of NHC-Pd/SBA-16-IL. These

Table 3 The Heck reaction in the presence of NHC-Pd/SBA-16-IL[a]



Entry	R	Z	Temperature/°C	Time/h	Isolated yield (%)
1	H	Ph	140	40	94
2	4-COMe	Ph	130	20	95
3	4-CHO	Ph	130	20	94
4	4-CN	Ph	130	24	97
5	4-NO_2	Ph	130	18	84
6	4-Me	Ph	140	46	82
7	4-COMe	CO_2Me	130	11.5	76
8	2-CN	CO_2Me	130	23	86
9	4-NO_2	CO_2Me	130	20	86

[a] The reaction was carried out with 4 mmol of halide, 4.2 mmol of styrene (or methyl acrylate), 4.6 mmol of NaOAc, 0.01 mol% Pd with respect to aryl bromides, and 3.5 mL of NMP under an N_2 atmosphere.

results further confirmed the high recyclability of NHC-Pd/SBA-16-IL.

Conclusions

By grafting the *N*-heterocyclic carbene palladium complex on the surface of the nanocages modified with ionic liquids, an efficient and highly recyclable heterogeneous catalyst for the Suzuki and Heck reactions was successfully prepared. The developed heterogeneous catalyst showed high activity for various aryl bromides and afforded a complete conversion of the unactivated bromobenzene even at a catalyst loading of 0.01 mol%. It could be easily recovered by a filtration and a good yield was obtained even after the catalyst was reused ten times. Its recyclability was much better than that of the catalyst prepared from amorphous silica under the same conditions. The significantly enhanced recyclability may be attributed to the isolated nanocages of SBA-16 which could efficiently prevent the aggregation and agglomeration of Pd particles formed during the catalytic reaction into the less active large particles, as evidenced by TEM. The strategy for stabilizing metal nanoparticles using isolated nanocages may be applied to other catalytic systems, in which the aggregation of metal nanoparticles is desired to be prevented.

Experimental

Reagents and materials

Pluronic P123 copolymer ($EO_{20}PO_{70}EO_{20}$), Pluronic copolymer F127 ($EO_{106}PO_{70}EO_{106}$) and $Pd(OAc)_2$ were purchased from Sigma Company. Tetraethyl orthosilicate, *N*-methylpyrrolin-2-one (NMP, distilled before using), 1-methylimidazole, phenylboronic acid, styrene, methyl acrylate and various aryl bromides were obtained from Shanghai Chemical Reagent Company of Chinese Medicine Group, (3-chloropropyl)trimethoxy silane was from Jianghan Fine Chemical Company (China, distilled before using). Amorphous silica gel with a specific surface area of 328 $m^2\ g^{-1}$ was obtained from Qidao Haiyang Chemical Plant. Mesoporous material SBA-15 was synthesized according to the reported procedure (specific surface area: 850 $m^2\ g^{-1}$; BJH pore diameter: 8.0 nm).[10]

Mesoporous cage-like material SBA-16 was synthesized according to the modified method.[7] A mixture of Pluronic F127 ($EO_{106}PO_{70}EO_{106}$, 7.42 g) and Pluronic P123 ($EO_{20}PO_{70}EO_{20}$,

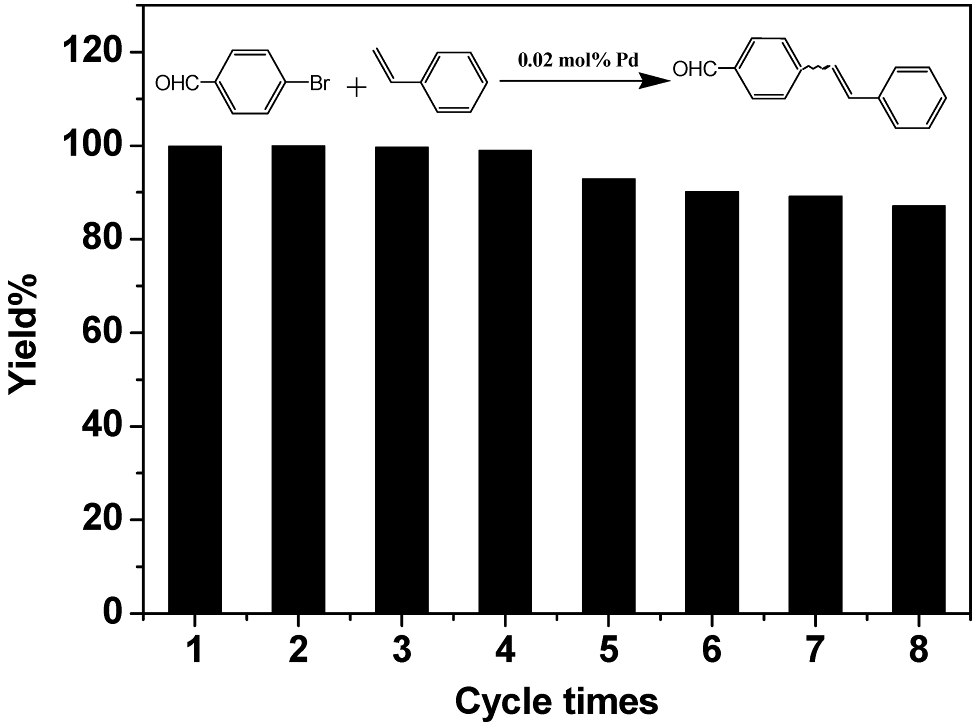


Fig. 10 Recycling test of NHC-Pd/SBA-16-IL with the Heck reaction, reaction times from 16 to 49 h.

1.19 g) was 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. After 4 h, 28 mL of tetraethyl orthosilicate was dropwise added to the solution. After being stirred for 40 min, the resultant suspension was transferred into autoclaves. The autoclaves were placed under static conditions at 308 K for 24 h. Afterward, the temperature of the autoclaves was raised up to 373 K and held for 32 h. After the hydrothermal treatment, the precipitated solid was isolated by a filtration and dried at 373 K for 24 h, yielding white solid powders. This powder 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 *N*-3-(3-trimethoxysilylpropyl)-3-methyl imidazolium chloride (ionic liquid)[11]

In a dry flask, (3-chloropropyl)trimethoxy silane (24.23 g) was added to 1-methylimidazole (10.12 g), and then the system was evacuated and purged with N_2 five times. After being stirred at 90 °C for 48 h under N_2 atmosphere, the resulting mixture was allowed to cool down to room temperature, was washed with dry ethyl acetate four times and dried under vacuum for 24 h at room temperature. The finally obtained ionic liquid was a kind of yellowish sticky liquids. The ^1H NMR spectral data for the ionic liquid is as follows: $\delta = 10.1$ (s, 1H), 7.3–7.6 (m, 2H), 3.8–3.9 (m, 5H), 3.59 (s, 9H), 1.81(m, 2H), 0.69 (m, 2H).

Preparation of a solution of *N*-heterocyclic carbene palladium complex (NHC-Pd) in ionic liquid[4b]

In a well-dried flask, $Pd(OAc)_2$ (0.0368 g) was added to the synthesized ionic liquid (0.7350 g). The system was evacuated and purged four times with N_2. The mixture was stirred at 60 °C for 12 h and then at 100 °C for 4 h under N_2 atmosphere. The system was attached to the vacuum system for 2 hours to remove the acetic acid and was then allowed to cool down to room temperature, affording a pale green-yellow solution of NHC-Pd complex in ionic liquid. In order to confirm the structure of the *N*-heterocyclic carbene palladium complex, *N*-heterocyclic carbene palladium complex was prepared from the ionic liquid and $Pd(OAc)_2$ (the molar ratio of them was 2 : 1) in DMSO. The ^1H NMR spectral data for the complex is as follows: $\delta = 7.3$–7.4 (m, 2H); 3.4–4.0(m, 11H), 1.90 (m, 2H), 0.63 (m, 2H).

The passivation of the external surface silanols of SBA-16

The passivation of the silanols on the external surface of SBA-16 was performed according to the reported procedure with some variations.[9] 3.0 g of SBA-16 (dried at 135 °C for 6 h) was dispersed into 50 mL of dry tetrahydrofuran (THF), and then 0.2 mmol of diphenyldichloro silane (Ph_2SiCl_2) was added into the system under N_2 atmosphere. After refluxing for 20 min, the solid was isolated by a filtration and washed with dry THF. The obtained solid was again dispersed into 50 mL of dry THF, and then 0.2 mmol of Ph_2SiCl_2 was added into the system under N_2 atmosphere. After refluxing for 30 min, the solid was isolated by a filtration and thoroughly washed with dry THF, resulting in SBA-16 with passivation.

Immobilization of *N*-heterocyclic carbene palladium complex and ionic liquid on SBA-16

The above solution of NHC-Pd complex in ionic liquid was diluted with dry $CHCl_3$ (13 mL). Into this solution 1.7 g of SBA-16 with passivation was added under a N_2 atmosphere. The resulting mixture was refluxed for 32 h. After being cooled, the solid material was isolated by a filtration and was repeatedly washed with $CHCl_3$, and then dried under vacuum overnight to give *N*-heterocyclic carbene palladium complex and ionic liquid immobilized on SBA-16. The resulting sample was denoted as NHC-Pd/SBA-16-IL. The Pd content in NHC-Pd/SBA-16-IL determined by ICP-AES was 0.23 wt%. The N and C content in NHC-Pd/SBA-16-IL determined by elemental analysis was 2.65 wt% and 9.95 wt%, respectively.

For comparison, *N*-heterocyclic carbene palladium complex and ionic liquid were immobilized on SBA-15 and amorphous silica through the same procedures. The resultant catalysts were denoted as NHC-Pd/SBA-15-IL and NHC-Pd/silica-IL. The Pd contents in NHC-Pd/SBA-15-IL and NHC-Pd/silica-IL determined by ICP-AES were 0.28 wt% and 0.13 wt%, respectively.

Typical procedures for the Suzuki reaction

A mixture of aryl bromides (4 mmol of halide), phenylboronic acid (4.4 mmol), $K_3PO_4\cdot 3H_2O$ (4.4 mmol), ethanol (4 mL), H_2O (4 mL), and NHC-Pd/SBA-16-IL (0.01 mol% equiv. to aryl bromide) was stirred at a given temperature for a given time. The reaction was monitored by TLC. After the reaction, the mixture was cooled down to room temperature and repeatedly extracted with diethyl ether (4 mL × 8). The combined organic layers were concentrated and the resulting product was purified by column chromatography on silica gel. The product was confirmed by ^1H NMR and melting point determination.

Recycling test for the Suzuki reaction was as follows: for the first run, the mixture of 32 mmol of bromobenzene, 35.2 mmol of phenylboronic acid, 35.2 mmol of K_3PO_4, 0.02 mol% Pd with respect to bromobenzene, 32 mL of water and 32 mL ethanol was stirred at 50 °C. The reaction was monitored by TLC. At the end of the reaction the mixture 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. The fresh solvent and substrates were added, but the molar ratios of substrates and solvent to Pd remained the same as the first run.

Typical procedures for the Heck reaction

A mixture of aryl bromides (4 mmol of halide), styrene (4.2 mmol), NaOAc (4.6 mmol), NMP (*N*-methylpyrrolidin-2-one, 3.5 mL) and NHC-Pd/SBA-16-IL (0.01 mol% with respect to aryl bromide) was stirred at a given temperature for a given time under N_2 atmosphere. After the reaction, the mixture was cooled down to room temperature and the organic layer was isolated by a centrifugation. The remaining residue was washed with DMF and the organic layer was again isolated by centrifugation. The combined organic layers were poured into 100 mL of water, leading to a solid at the bottom of vessel. The solid state organic product was isolated by filtration, washed with water and dried. If necessary, the product was purified by column chromatography on silica gel. The product was confirmed by ^{1}H NMR and melting point determination.

Recycling test for the Heck reaction was as follows: for the first run, the mixture of 20 mmol of 4-bromobenzaldehyde, 21 mmol of styrene, 23 mmol of NaOAc, 17.5 mL of NMP and 0.02 mol% Pd with respect to bromobenzene was stirred at 130 °C. The reaction was monitored by TLC. At the end of the reaction the mixture was cooled down to room temperature and the catalyst was isolated by a centrifugation. The resulting catalyst was washed with DMF, methanol and acetone in sequence and dried under vacuum. The recovered catalyst was weighed again. The fresh solvent and substrates were added, but the molar ratios of substrates and solvent to Pd remained the same as the first run.

Characterization and analysis

Small-angle X-ray powder diffraction was performed on Rigaku (Cu Kα, 40 kV, 30 mA). N_2 physical adsorption was carried out on a Micrometrics ASAP2020 volumetric adsorption analyzer (before the measurements, samples were degassed at 393 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/P_0 (above 0.99). Pore diameters were determined from the adsorption branch using Barrett–Joyner–Halenda (BJH) method. FT-IR spectra were collected on Thermo-Nicolet-Nexus 470 infrared spectrometer. Pd content was analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES, AtomScan16, TJA Co.). C and N content analysis were conducted on a Vario EL (Elementar). X-Ray photoelectron spectroscopy (XPS) was recorded on a Perkin-Elmer 5400 ESCA and the C_{1S} line at 284.9 eV was used as the binding energy reference. TEM micrographs were taken using a JEM-2000EX transmission electron microscope at 120 kV. Solid state NMR spectra were obtained 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.

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

Biphenyl ($CDCl_3$, 300 MHz, ppm). 7.57 (d, 4H, J = 9 Hz); 7.41–7.46 (m, 4H); 7.34 (t, 2H, J = 7.5 Hz).

4-Biphenylcarbaldehyde ($CDCl_3$, 300 MHz, ppm). 10.07 (s, 1H); 7.95 (d, 2H, J = 7.8 Hz); 7.75 (d, 2H, J = 7.8 Hz), 7.43–7.66 (m, 5H).

4-Acetylbiphenyl ($CDCl_3$, 300 MHz, ppm). 8.06 (d, 2H, J= 6 Hz); 7.39–7.68 (m, 7H); 2.67(s, 3H).

4-Cyanobiphenyl ($CDCl_3$, 300 MHz, ppm). 7.53–7.64 (m, 4H); 7.50 (d, 2H, J = 7.8 Hz); 7.35–7.42 (m, 3H).

4-Nitrobiphenyl ($CDCl_3$, 300 MHz, ppm). 8.29 (d, 2H, J = 8.7 Hz); 7.73 (d, 2H, J = 8.7 Hz); 7.45–7.62 (m, 5H).

4-Methylbiphenyl ($CDCl_3$, 300 MHz, ppm). 7.52 (d, 2H, 6 Hz); 7.43 (d, 2H, 6 Hz); 7.37 (t, 2H, 6 Hz); 7.27 (d, 1H, 6 Hz); 7.21 (d, 2H, 9 Hz); 2.34 (s, 3H).

4-Methoxybiphenyl ($CDCl_3$, 300 MHz, ppm). 7.55–7.60 (m, 4H); 7.45 (t, 2H, J = 7.5 Hz); 7.33 (m, 1H); 7.00 (d, 2H, J = 9 Hz); 3.88 (s, 3H).

Stilbene ($CDCl_3$, 300 MHz, ppm). 7.46–7.52 (m, 4H); 7.27–7.39 (m, 6H); 7.16 (s, 2H).

4-Acetylstilbene ($CDCl_3$, 300 MHz, ppm). 7.94 (d, 2H, J = 9 Hz); 7.55 (m, 4H); 7.15–7.41 (m, 5H); 2.61 (s, 3H).

4-Formylstilbene ($CDCl_3$, 300 MHz, ppm). 10.01 (s, 1H); 7.87 (d, 2H, J = 8.4Hz); 7.66 (d, 2H, 8.1 Hz); 7.55 (d, 2H, J = 7.2 Hz); 7.13–7.43 (m, 5H).

4-Cyanostilbene ($CDCl_3$, 300 MHz, ppm). 7.52–7.29 (m, 5H); 7.29–7.41 (m, 4H); 7.21 (s, 1H); 7.11 (s, 1H).

4-Nitrostilbene ($CDCl_3$, 300 MHz, ppm). 8.21 (d, 2H, J = 9 Hz); 7.63 (d, 2H, J = 9 Hz); 7.55 (d, 2H, J = 6 Hz); 7.12–7.43 (m, 5H).

4-Methylstilbene ($CDCl_3$, 300 MHz, ppm). 7.52 (d, 2H, J = 6 Hz); 7.35–7.43 (m, 4H); 7.25–7.29 (d, 1H, J = 6 Hz); 7.18 (d, 2H, J= 9 Hz); 7.10 (s, 2H); 2.39 (s, 3H).

Methyl-4-acetylcinnamate ($CDCl_3$, 300 MHz, ppm). 7.96 (d, 2H, J = 8.0 Hz), 7.62–7.34 (m, 3H, J = 16.0 Hz), 6.54 (d, 1H, J = 16.0 Hz), 3.85 (s, 3H), 2.64 (s, 3H).

Methyl-2-cyanocinnamate ($CDCl_3$, 300 MHz, ppm). 7.96 (d, 1H, J = 15 Hz), 7.49–7.74 (m, 4H); 6.59 (d, 1H, J = 15 Hz); 3.84 (s, 3H).

Methyl-4-nitrocinnamate ($CDCl_3$, 300 MHz, ppm). 8.24 (d, 2H, J = 9 Hz), 7.69–7.74 (m, 3H); 6.54 (d, 1H, J = 15Hz), 3.84 (s, 3H).

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