



Monodisperse noble metal nanoparticles stabilized in SBA-15: Synthesis, characterization and application in microwave-assisted Suzuki–Miyaura coupling reaction

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ABSTRACT

A series of Pd and Pd/Au alloy nanoparticles (NPs) with narrow size distribution were encapsulated or stabilized by G4-poly (amido-amine) (G4-PAMAM, G represents the generation) planted in SBA-15. Monodisperse NPs are uniformly distributed in channels of SBA-15 as observed by TEM images. HRTEM, ICP and EDS results confirm the alloy structure of bimetallic NPs. A combination of N₂ adsorption–desorption analysis, ICP and GC was used to optimize the best amount of metal precursors to form catalysts. The as-prepared catalyst manifests outstanding activity and recyclability in microwave-assisted Suzuki–Miyaura coupling reaction when compared with commercial Pd/C. Meanwhile, Pd/Au alloy NPs exhibit higher activity than monometallic ones in catalyzing the coupling between aryl bromide/aryl chloride and arylboronic acid. The mechanism of the improvement of catalytic performance is discussed.

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1. Introduction

In the field of catalytic nanoparticles (NPs), the size dispersity, morphology and composition of active metals are of importance for the activity and selectivity of the catalysts [1–3]. The previously reported capping agents and protective polymers, which were used to stabilize NPs [4–6] have drawbacks in protecting metals under harsh catalytic reaction conditions. Dendrimers can act as hosts or stabilizers for either monometallic [7–11] or bimetallic [12–15] NPs, interestingly, such NPs are monodisperse and unlikely to aggregate after a long time, and consequently are competent to behave as catalysts. Scott et al. investigated catalytic activity of palladium [13] dendrimer-encapsulated nanoparticles (DENs) in hydrogenation reactions and found dendritic branches could adjust and control the access of substrates into the dendrimers [16]. Li and El-Sayed [17,18] also investigated the influence of dendrimer's generation on Pd colloidal NPs in Suzuki–Miyaura coupling reactions. They concluded that the encapsulation of Pd particles provided by G4-poly (amido-amine) (G4-PAMAM, G represents the generation) dendrimers led to a loss of catalytic activity, while G3 did a better job both on catalysis and on stabilizing NPs. But these types of catalysts had poor performance in catalyzing the coupling between arylboronic acid and aryl bromides because of

homo-coupling of aryl bromides, the same as the finding of Pittelkow et al. [19].

Introducing another metal into pure Pd NPs is a promising method to improve catalytic activity. In recent years, Pd/Au bimetallic system has been widely explored. For example, the bimetallic NPs have shown excellent catalytic performance for the direct synthesis of H₂O₂ from H₂ and O₂ [20–22]. In Hutchings' group, Pd/Au catalysts manifested a dramatic increase in activity for the oxidation of alcohols to aldehydes when compared to pure Au or Pd catalysts [23]. Additionally, the catalysts have been used in the hydrochlorination of acetylene [24], hydrodesulfurization of thiophene [25] and other reactions [26–29]. To the best of our knowledge, although palladium NPs have been studied intensively in Suzuki–Miyaura coupling reaction, the employment of Pd/Au alloy in the same reaction has not been reported in literatures. For this reason, it is desirable to fabricate heterogeneous Pd/Au alloy catalysts (stabilized in SBA-15) and investigate their catalytic performance in Suzuki–Miyaura coupling reaction.

Moreover, in Suzuki–Miyaura coupling reaction, Glasspoole et al. found aqueous base was highly detrimental to the structure of silica-related catalysts, which can be avoided by using boric acid or aluminum-doped material [30]. In this paper, microwave-assisted technique is another way to optimize catalysts and improve catalytic activity. In recent literatures, microwave-assisted Suzuki coupling was almost confined in homogeneous reaction in solutions; few examples were reported involving catalyst existing in solid phase, except the research of Baxendale et al. [31].

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Herein, we will describe a facile method to synthesize size-controllably (1–3 nm) monodisperse Pd and Pd/Au bimetallic NPs stabilized in SBA-15, which can be easily used in microwave-assisted Suzuki–Miyaura coupling reactions. To optimize the as-prepared catalysts, microwave-assisted Suzuki coupling reactions between iodobenzene and arylboronic acid were employed to test catalytic activity and stabilization. Moreover, Pd/Au alloy nanoparticles with similar metal loading exhibit higher activity than monometallic ones in catalyzing the coupling between aryl bromide/aryl chloride and arylboronic acid. The mechanism of the improvement in catalytic performance of this kind of materials was studied by XPS measurement.

2. Experimental

2.1. Synthesis of catalyst

Mesoporous silica SBA-15 hard templates were prepared under hydrothermal conditions of 120 °C for 48 h according to the established procedures [32]. Then, four consecutive repetition of a Michael-type addition reaction and amidation of ester moieties produced G4-PAMAM planted in the channels of SBA-15 [33,34]. The resulting powder solids were tested to roughly determine the number of dendrimers before complexation with metal ions.

Briefly, 0.1 g of white powder was dispersed under stirring in 50 ml of HCl aqueous solution (pH = 2). Then, 5, 10, 20, 30 and 40 equiv. (compared with calculated number of dendrimers) of a freshly prepared K_2PdCl_4 (99.99%, Alfa Aesar) aqueous solutions were added dropwise. After stirring for 12 h, the yellow solid was centrifugally separated and sonic oscillated for no less than three times before dried at 50 °C. The resulting powder was denoted as $Pd^{2+} x$ -G4-PAMAM-SBA-15, where x referred to the metal precursors/dendrimer molar ratio. The metal complexation was reduced by at least 10-fold molar excess of $NaBH_4$ from a freshly prepared aqueous stock solution. Finally, the catalyst was obtained by centrifugal separation and dried in vacuum. The obtained sample was denoted as Pd_x -G4-PAMAM-SBA-15. Pd_5Au_5 -G4-PAMAM-SBA-15 was prepared through above-mentioned procedure but with the addition of chloroauric acid tetrahydrate (purchased from Sinopharm Chemical Reagent Co., Ltd.) later than Pd by 11.5 h, followed by stirring for 30 min.

2.2. Microwave-assisted Suzuki reaction between iodobenzene and arylboronic acids

In a typical procedure (e.g., reaction catalyzed by Pd_x -G4-PAMAM-SBA-15), 0.5 atom% Pd catalyst and 3 equiv. (3 mmol) of K_3PO_4 and 1.2 mmol of arylboronic acid (purchased from Alfa Aesar) were added to an N_2 bubbling solution (3 ml) of H_2O /ethanol ($v/v = 3:2$) with magnetic stirring. Then, 1 mmol of iodobenzene (98%, Alfa Aesar) was dropped into the reaction vial. After sealed up, the reaction was irradiated in a microwave apparatus (Initiator 8 Exp, from Biotage) at 100 °C for 30 min. After cooling down to ambient temperature, the reaction mixture was purified by column chromatography (silica gel/hexane) to give the desired products.

2.3. Microwave-assisted Suzuki reaction between bromoarenes and arylboronic acids

The co-solvent was the same as above-mentioned. Briefly, 1% molar equiv. of Pd or Pd/Au alloy catalyst and 3 equiv. (3 mmol) of K_3PO_4 and 1.05 mmol of arylboronic acids were added to an N_2 bubbling solution (3 ml) with magnetic stirring. Then, 1 mmol of bromoarene (purchased from TCI) was added into the reaction

vial. After sealed up, the reaction was irradiated in a microwave apparatus at 100 °C for 30 min.

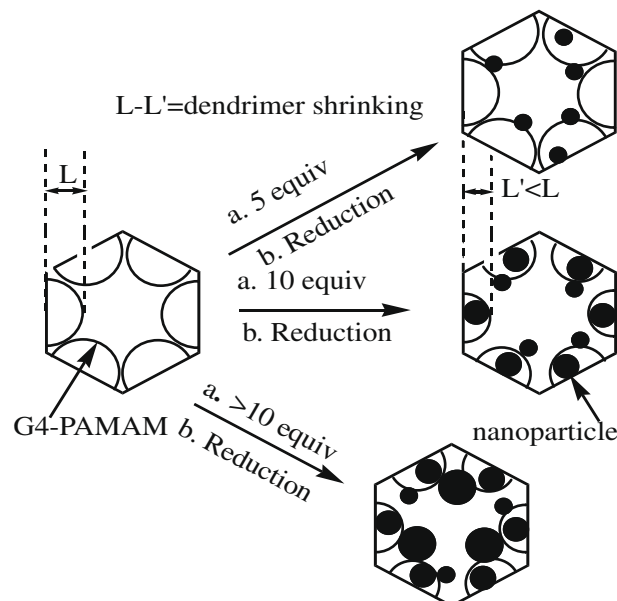
2.4. Characterizations

The nitrogen contents of the G4-PAMAM-SBA-15 were determined by elemental analyses carried out on a Vario EL III analyzer. Nitrogen adsorption–desorption isotherms at 77 K were obtained with a Micromeritics ASAP 2000 apparatus. The samples were previously degassed under vacuum at 50 °C for 24 h. Surface areas, pore volume and pore sizes were determined by the BJH method applied to the adsorption branch of the isotherms. The shape and structure of catalyst were analyzed on a JEOL 2010 transmission electron microscope (TEM). The samples were prepared by placing a drop of catalyst sol in ethanol onto a continuous carbon-coated copper TEM grid. Inductively coupled plasma (ICP) analysis of catalyst and residual aqueous phase after extraction was performed on an Ultima 2 analyzer (Jobin Yvon). X-ray photoelectron spectroscopy (XPS) measurements were analyzed on coated alumina using a Physical Electronics PHI-Quantum 2000 Scanning ESCA Microprobe. UV–vis spectra were obtained using a Lambda 35 UV–visible spectrophotometer. 1H and ^{13}C NMR spectra were recorded on an AVANCE III Nuclear Magnetic Resonance Spectrometer (BRUKER BIOSPIN) with deuterated chloroform as the internal reference. Yields of cross-coupling reactions were determined on VARIAN 430 Gas Chromatograph.

3. Results and discussion

3.1. Structural characteristics of the Pd and Pd/Au alloy NPs

To obtain monodisperse NPs, the previous method described by Gao and coworker [33] was modified. To roughly fix the number of dendrimers, we suppose that they are all integrated as a half-G4-PAMAM. Because G4-PAMAM has a globular configuration [35], dendrimers immobilized in channels are deduced to be hemisphere (as shown in Scheme 1). Consequently, the number of dendrimers can be calculated based on a certain molar ratio of N atoms to half-G4-PAMAM (61:1) [36]. Figs. 1 and S1 display the TEM images of Pd_5 -G4-PAMAM-SBA-15, the other Pd_n -G4-PAMAM-



Scheme 1. The proposed procedure for preparation of catalysts (a, the number represents the molar ratio of Pd^{2+} /dendrimers and b, the reductant is $NaBH_4$).

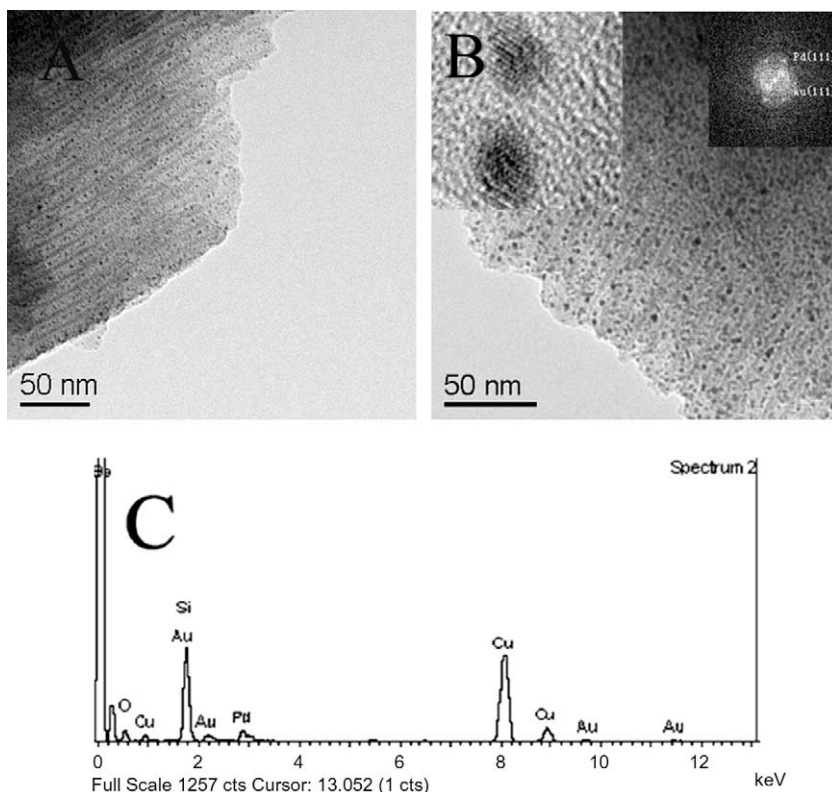


Fig. 1. TEM images of (A) Pd₅-G4-PAMAM-SBA-15, (B) Pd₅Au₅-G4-PAMAM-SBA-15 (the left insert is the HRTEM image displaying the lattice fringes of the randomly selected two NPs, and Fourier diffractogram shown in the right insert discloses spots corresponding to Pd/Au alloy NPs), and (C) EDS spectra of the two selected NPs.

SBA-15 ($n = 10, 20, 30$ and 40) and the corresponding size distribution. Evidently, highly dispersive NPs are indeed stabilized in pores of SBA-15, with average size and size distribution in 1.6 ± 0.4 nm, 1.9 ± 0.4 nm, 2.3 ± 0.4 nm, 2.4 ± 0.4 nm and 2.5 ± 0.4 nm, respectively. The average diameter of palladium particle is smaller than the pore size (about 7 nm) of SBA-15, indicating the accessible metal sites in the pores.

Attracted by the superior catalytic performance of bimetallic NPs compared with monometallic ones, great efforts have been put into the formation of the former. Although TiO₂ [23], alumina sols [25] and hydroxyapatite [37] have been applied to stabilize bimetallic NPs, the works using regular-structured silica as stabilizer are few. In this work, stable Pd/Au bimetallic NPs were obtained in SBA-15 planted by dendrimer (see below). Controlling the contact time between [AuCl₄]⁻ and dendrimers within 30 min is of importance for the formation of highly dispersive Pd/Au NPs, otherwise Au³⁺ ions are firstly reduced into Au particles before reduction with NaBH₄ to lead a wine red system [38] (see Fig. S2). Similar to palladium NPs, the bimetallic NPs are clearly distributed in the channels, with average diameter in about 1.5 nm. To understand the structure of NPs, we randomly selected two particles as shown in the top left inset in Fig. 1B. The HRTEM image shows spherical structure with distinct lattice fringes. The Fourier diffractogram obtained from these two NPs as marked in the top right inset of Fig. 1B clearly shows two sets of spots characteristics of Pd and Au, which are Pd(111) lattice spacing of 0.225 nm (JCPDS card 46-1043) and Au(111) plane with 0.235 nm (JCPDS card 04-0784) [39], respectively. In addition, the EDS analysis (Fig. 1C) of the two particles obviously gives the peaks of palladium and gold, and the spectra superimpose with those obtained for all NPs in Fig. 1B. These results confirm that the Pd/Au alloy NPs were obtained and stabilized in the channels of SBA-15 planted by dendrimer.

3.2. Analysis of different palladium catalysts

Previous studies have shown that the diameter distribution of Pd particles (G4-OH (Pd₁₀)) is only 1.4 ± 0.4 nm [17]. So we suspect that the confinement of cavities for our dendrimers may not be as effective as the one in G4-PAMAM reported previously [13,16,17]. Probably, the number of our dendrimers in SBA-15 is less than expected; or, the dendrimers are not as integrated as half-G4-PAMAM. The elemental analysis (EA) of *Gn*-SBA-15 (Table S1) confirms the earlier two conclusions in more detailed way, indicating the formation of dendrimers at every step is imperfect. Interestingly, although the dendrimers planted in channels may fall short of expectations in quantity or quality, they show good ability to cap metal particles when the amount of precursor was properly controlled.

For simplification, we suppose the dendrimers planted in SBA-15 are hemispheric in shape. It was suggested that, since the diameter of G4-PAMAM is only 4.5 nm [40], the hemisphere radius is about 2.2 nm. We deduce the NPs with diameter larger than 2.2 nm may not be effectively encapsulated in dendritic cavity; instead, they may be just stabilized by dendrimers with peripheral groups. The semiquantitative analysis of pore volume (Fig. 2) provided by nitrogen adsorption-desorption with the BJH method proves the conclusion in another way.

It was reported that by judicious controlling of pH value (pH = 2), the terminal amino groups of NH₂-terminated PAMAM dendrimers were selectively protonated [41,42], and the noble metal ions were inclined to complex with interior tertiary amine groups of the dendrimers to provide a mean for encapsulation of noble metal NPs through reduction [43]. Our G4 dendrimers are not integrated as expected, and some of the terminal groups may not be amino, when the pH is adjusted to 2, the non-amino terminal groups may capture Pd ions through the interaction between

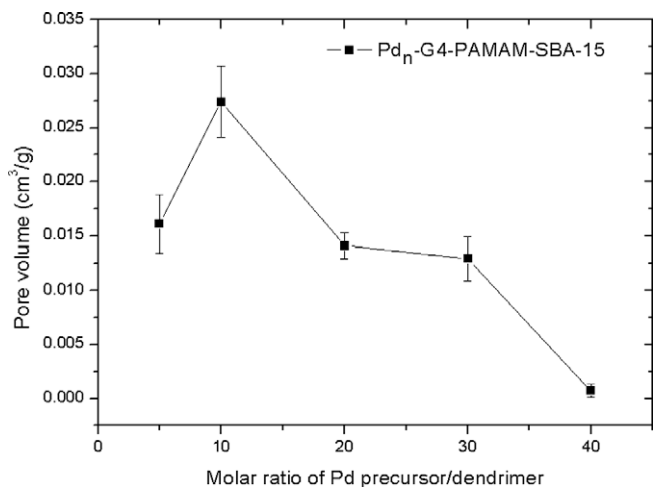


Fig. 2. Molar ratio of Pd precursor/dendrimers vs. pore volume (average value of three repeated tests).

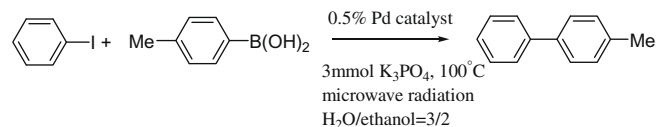
Pd ions and such groups to lead to the existence of Pd NPs at the periphery of the dendrimers after reduction [36], and the efficient pore volume of Pd₅-G4 (Fig. 2) is smaller than that of G4 (0.02 cm³/g). When increasing the ratio of Pd²⁺/dendrimer to 10, the interactions between Pd²⁺ and the non-amino terminated group may be saturated and more Pd²⁺ ions penetrate into the dendrimer through the complexation between Pd²⁺ and interior tertiary amine groups to lead to “dendrimer shrinking” after reduction, and the efficient pore volume of Pd₁₀-G4 (~0.03 cm³/g) is larger than that of G4. Further increasing the ratio of Pd²⁺/dendrimer to 20 or more will lead to the saturation of the complexation between Pd²⁺ ions and the interior tertiary amine groups, and more Pd NPs will exist at the periphery of the dendrimers to give rise to smaller pore volumes than that of G4. Meanwhile, from TEM observations (see Fig. 1A and B), no palladium aggregations are formed outside the channels, indicating there are no free metal ions existing before reduction; no NPs can be observed except in SBA-15, indicating almost all the dendrimers are firmly planted in channel instead of dissociated into aqueous phase in the procedure of formation of catalysts. The formation of the NPs catalysts is demonstrated in Scheme 1.

3.3. Microwave-assisted Suzuki–Miyaura reactions

In recent years, thousands of organic reactions including Suzuki coupling are improved both in catalytic activity and in time reduction due to microwave-assisted technique [31]. To evaluate the microwave-assisted reaction, we carried out comparative synthesis involving Pd₁₀-G4-PAMAM-SBA-15 catalyzed coupling between iodobenzene and benzeneboronic acid, heated by conventional method and microwave radiation. The solvent (water/ethanol = 3:2) was heated with 1 mmol of iodobenzene, 1.2 mmol of benzeneboronic acid, 0.5% mol of catalyst and 3 equiv. of K₃PO₄ at 100 °C. In conventional condition, reaction after 8 h gave product in 97% yield for 1st cycle and 31% for the 2nd cycle. But the microwave radiation afforded 97% yield for only 10 min, which indicated 48-fold rate increase, and the reactions were completed after 30 min. To clarify the influence of catalyst in microwave-assisted Suzuki reaction, reaction without catalyst under radiation was carried out under the same condition and almost no product was obtained, demonstrating that microwave can only promote the reactions in the presence of the catalyst.

To investigate the catalytic activity and stability of the five prepared Pd NPs catalysts, the following experiments were per-

formed. The iodobenzene was coupled with 4-methylbenzeneboronic acid in the presence of catalysts (0.5 mol% of metal), following the condition in Scheme 2. It can be seen from Fig. 3 that the yields of Suzuki coupling for iodobenzene in the presence of the five catalysts generally decreases as the Pd²⁺/dendrimer ratio increases: 98% for Pd₅-G4-PAMAM-SBA-15, 97% for Pd₁₀-G4-PAMAM-SBA-15, 92% for Pd₂₀-G4-PAMAM-SBA-15, 78% for Pd₃₀-G4-PAMAM-SBA-15 and 80% for Pd₄₀-G4-PAMAM-SBA-15, respectively. On the other hand, the curve for residual content of Pd in



Scheme 2. Cross-coupling between iodobenzene and 4-methylbenzeneboronic acid.

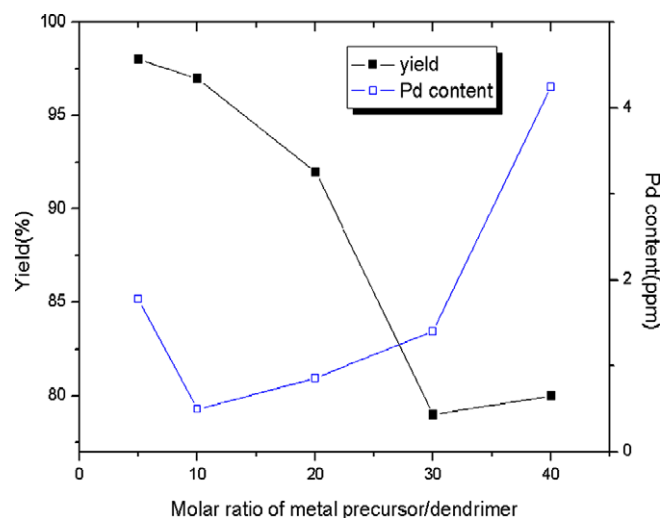


Fig. 3. Variation of yields (determined by GC) and residual content of Pd in reaction medium (determined by ICP-AES) vs. molar ratio of metal precursor/dendrimer.

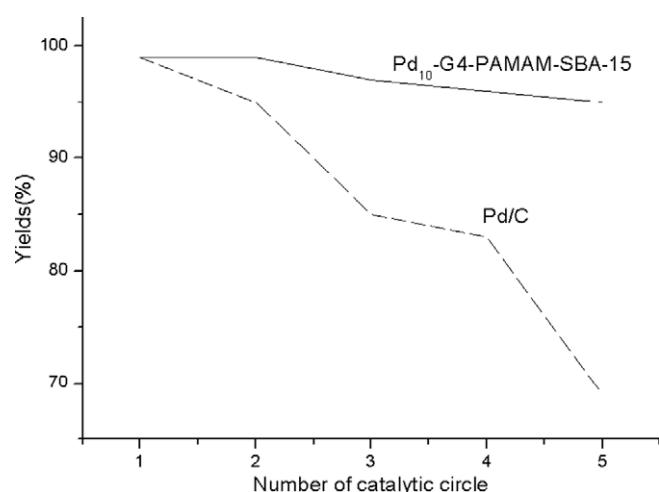


Fig. 4. Yields (determined by GC) vs. the number of catalytic cycle for Pd₁₀-G4-PAMAM-SBA-15 and Pd/C.

Table 1
Product and yields for Suzuki coupling reactions between arylboronic acids and iodobenzene catalyzed by Pd₁₀-G4-PAMAM-SBA-15 (0.5 mol% of metal) in 3:2 H₂O/ethanol (base, K₃PO₄; temp., 100 °C; time, 30 min).

Entry	Arylboronic acid	Product	Yield (%) ^a
1			97
2			>99
3			90
4			83
5			68
6			31

^a Determined by GC analysis.

reaction medium (determined by ICP) after reaction goes in an opposite direction, except for Pd₅-G4-PAMAM-SBA-15: 1.8 ppm for Pd₅-G4-PAMAM-SBA-15, 0.4 ppm for Pd₁₀-G4-PAMAM-SBA-15, 0.8 ppm for Pd₂₀-G4-PAMAM-SBA-15, 1.4 ppm for Pd₃₀-G4-PAMAM-SBA-15 and 4.3 ppm for Pd₄₀-G4-PAMAM-SBA-15, respectively. Although the activity for Pd₅-G4-PAMAM-SBA-15 is the highest, its stability is poor (also seen in Fig. S3). Combining the activity and stability of the five catalysts, the ratio of 10 for Pd²⁺/dendrimer may be the optimized ratio for the fabrication of our Pd NPs catalyst.

As shown in Fig. 4, when Pd₁₀-G4-PAMAM-SBA-15 was applied to coupling between iodobenzene and benzenboronic acid, the yield in the 5th cycle is 95%, indicating only a slight loss of the catalytic activity. However, when the commercial Pd/C is applied in the reaction, dramatic loss of catalytic activity is observed in the 5th cycle (the yield of coupling product is only 69%). Furthermore, it is found that air has little influence on the reaction because the procedure without N₂ bubbling also gives 96% yield, which is as high as that using N₂. Note: a mild base is needed for this reaction otherwise the SBA-15 holding dendrimers disappears in solvent. The results indicate that Pd₁₀-G4-PAMAM-SBA-15 catalyst is very stable and can be recycled and reused easily.

The substrate selectivity is also a function of dendrimers [40], because higher generation dendrimers are less porous, which limits access of substrate to the encapsulated NPs. To test and verify this conclusion reported by others, we designed a series of coupling reaction between iodobenzene and several arylboronic acids. Oxidative addition between iodobenzene and noble metal is rate-determining step during Suzuki reaction [44]. Furthermore, the step involving arylbenzene acids is supposed to occur at surface of NPs [45]. So we fix up a variation by using only one kind of ben-

zene halide–iodobenzene, to focus on the access of substrates. The results (Table 1) show that *para*-substituted arylboronic acids (regardless of activated or passivated) facilitate coupling to afford high yields, whereas the *ortho*-substituted molecules have difficulty in penetrating through dendrimers to interact with NPs to give poor yield.

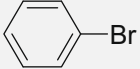
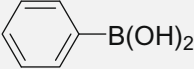
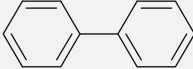
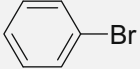
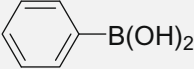
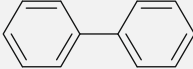
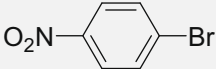
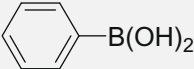
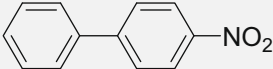
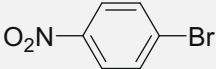
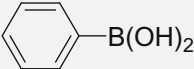
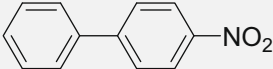
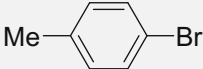
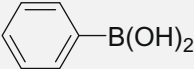
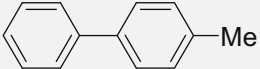
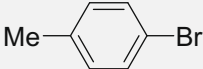
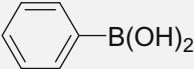
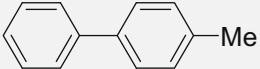
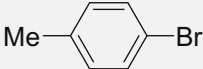
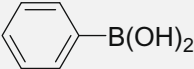
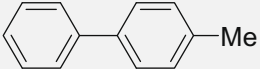
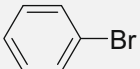
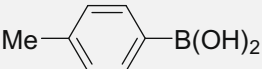
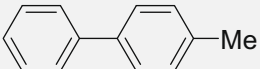
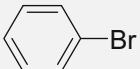
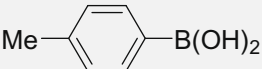
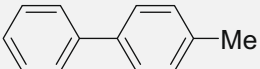
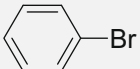
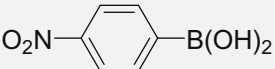
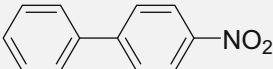
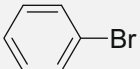
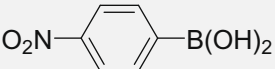
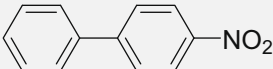
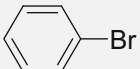
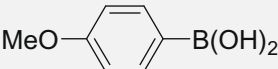
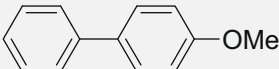
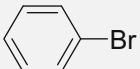
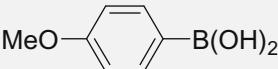
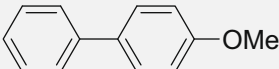
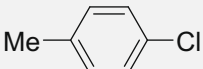
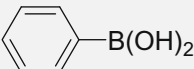
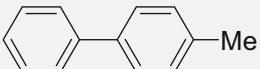
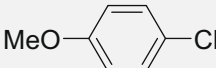
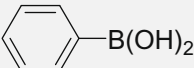
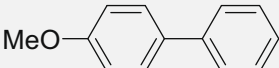
It was reported that the coupling between arylboronic acids and aryl bromides is much slower than the reactions between arylboronic acids and aryl iodides. Low yields were always due to byproducts resulting from homo-coupling of aryl bromides [18,19]. Unfortunately, in spite of microwave-assisted technique the same poor performance was observed in the presence of Pd₁₀-G4-PAMAM-SBA-15, as shown in Table 2 (entries 1, 3, 5, 8, 10 and 12). To improve the coupling reactivity, the Pd/Au alloy NPs catalyst was applied in the reaction. It can be seen from Table 2 (entries 2, 4, 6, 9, 11 and 13), Pd/Au NPs with similar metal loading display superior activity than pure palladium NPs, with higher yields in general. The bimetallic NPs can also catalyze coupling between aryl chloride and arylboronic acid with relatively high yields (entries 14 and 15).

3.4. XPS characterization of palladium and Pd/Au alloy NPs

XPS was employed to investigate the mechanism of the improvement of catalytic performance of Pd/Au alloy NPs. XPS provides information about the Pd oxidation state in palladium and Pd/Au alloy NPs because photoelectrons with energies of 337 eV (Pd_{5/2}) and 342 eV (Pd_{3/2}) correspond to Pd²⁺, and those at 335 eV (Pd_{5/2}) and 340 eV (Pd_{3/2}) correspond to metallic Pd⁰ [46]. In Fig. 5, the peaks for Pd⁰ are observed for both Pd and Pd/Au alloy catalysts, while those for Pd²⁺ is observed only in pure Pd catalyst, illustrating the presence of Pd²⁺ ions in pure Pd catalyst but not in

Table 2

Products and yields for Suzuki coupling reactions between arylboronic acids and aryl bromides catalyzed by Pd NPs and Pd/Au NPs (0.5 mol% of metal) in 3:2 H₂O/ethanol (base, K₃PO₄; temp., 100 °C; time, 30 min).

Entry	Aryl halides	Arylboronic acid	Catalyst	Product	Yield (%) ^a
1			Pd ₁₀		21
2			Pd ₅ Au ₅		78
3			Pd ₁₀		33
4			Pd ₅ Au ₅		90
5			Pd ₁₀		13
6			Pd ₅ Au ₅		58
7			Au ₅		Trace
8			Pd ₁₀		32
9			Pd ₅ Au ₅		92
10			Pd ₁₀		8
11			Pd ₅ Au ₅		10
12			Pd ₁₀		56
13			Pd ₅ Au ₅		64
14			Pd ₅ Au ₅		55
15			Pd ₅ Au ₅		43

^a Determined by GC analysis.

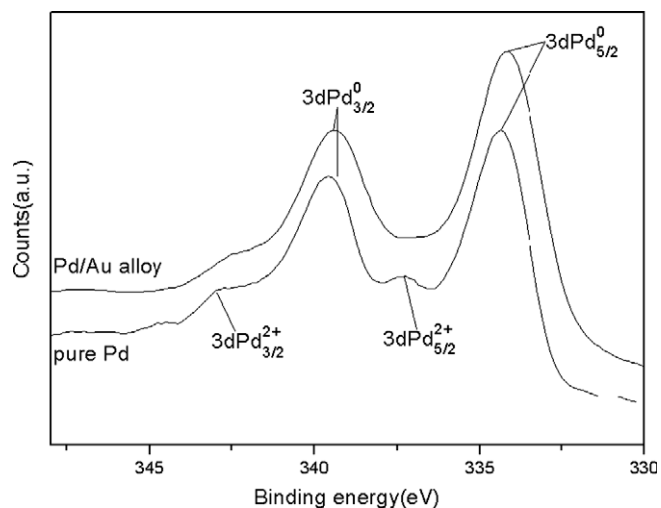


Fig. 5. XPS spectra of pure palladium and Pd/Au alloy catalysts.

Pd/Au alloy catalyst. Previous reports [16,24] found that only partial of metal ions were reduced by NaBH₄ because metal ions would form complexes with Cl⁻, H₂O and the internal amine groups of the dendrimer. In Pd/Au alloy system, although pure gold has no catalytic activity in Suzuki cross-coupling reaction (entry 7, Table 2), the presence of Au³⁺ in dendrimer before reduction may lower the complexation between Pd²⁺ and internal amine groups or other groups, leading to the complete reduction of Pd²⁺ to Pd⁰. This induces the higher catalytic activity of Pd/Au alloy catalyst

than that of Pd catalyst, because Pd⁰ is the active state for Suzuki cross-coupling reaction.

4. Summary and conclusions

Pd and Pd/Au alloy NPs catalysts have been successfully prepared by controlling pH value, amount of precursors and contact time between metal ions and SBA-15 supported dendrimers. The TEM images indicate that the NPs are nearly monodisperse in size and stabilized in channels of SBA-15 planted by dendrimers. The Pd NPs catalysts manifest outstanding activity and recyclability in Suzuki–Miyaura coupling reaction when compared with commercial Pd/C, and the Pd₁₀-G4-PAMAM-SBA-15 catalyst is the best one. Meanwhile, Pd/Au alloy NPs exhibit higher activity than monometallic ones.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jcat.2010.01.004](https://doi.org/10.1016/j.jcat.2010.01.004).

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