



Cyclopalladated ferrocenylimine functionalized polymer brushes film and its mechanism investigation of heterogeneous catalysis



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ABSTRACT

A highly active, reusable and stable cyclopalladated ferrocenylimine functionalized polymer brushes film (**Pd/PBs**) had been developed. The **Pd/PBs** was tested in Suzuki reaction and displayed high activity for the preparation of various biaryls at elevated temperatures in neat water without ligands. Good reusability and stability were presented as that catalytic film could be reused at least eight times with little Pd leaching into the crude product. The reasonable and feasible reaction mechanism of the heterogeneous Suzuki reaction was deeply explored, in which a catalytic cycle of Pd^{II} to Pd⁰ and Pd⁰ to Pd^{II} on the surface was clearly detected and illustrated. In this approach, the coupling reaction catalyzed by active Pd species on the surface of nano-films had proceeded via a mechanism of surface-catalyzed process.

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1. Introduction

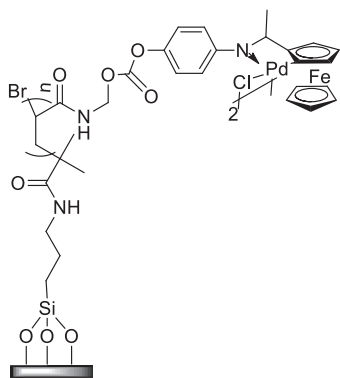
Heterogeneous catalytic reactions play important roles not only in the research laboratory but also in the chemical and pharmaceutical industries [1]. They are classified according to the supports involved, such as organic, hybrid organic–inorganic, inorganic supports [2]. Although numerous heterogeneous catalysts are known and used in industry, there are still some problems to solve, such as the high loading of catalysts, high reaction temperature, addition of organic solvents, and leakage of the catalyst into the reaction media [3]. The mechanistic study is certainly one of the most striking weaknesses of current studies in heterogeneous catalysis [4]. In general, it can be anticipated that much help in improving the catalytic systems will come from a careful examination of the intimate mechanisms on the solid through combined methods. Therefore, discovery of novel supports originating from renewable resources will be a key point in the context of sustainable chemistry, and development of suitably sensitive analytical methods constitutes another research priority. Various analytical methods can characterize, identify, and estimate the nature of the surface species, enabling thin films [5] (Langmuir–Blodgett films, self-assemble film, etc.) to be an ideal model system to study the surface and interface behavior, with which we can investigate catalytic

behavior and mechanisms at molecular level which is suitable to study the heterogeneous catalysis.

Polymer brushes with versatile molecular constructions for shaping surface properties are vital in areas such as nanotechnology, biosensors, and biomedical sciences [6]. Polymer brushes on nano-materials have been used for controlling colloidal stability, improving matrix compatibility in nanocomposite fabrication and controlling particle self-assembly, while brush-coated porous substrates can be used as highly selective membranes [7]. Grafting of polymer onto solid surfaces is an effective means to improve surface properties as the surface grafted polymer chain can interfere with the aggregation of these particles and increase their surface affinity for organic solvents and polymer matrix, thereby leading to better dispersion [8]. The dynamic nature of the polymer brushes together with the particularly high local concentrations engendered with such frameworks offer unique opportunities in supported catalysis, which can be used to achieve high catalyst loadings while allowing good accessibility to the active sites [9]. Our idea is to immobilize solid catalysts on the surface of solid substrates through polymer brushes and then to evaluate the activity and recyclability of the resulting composites. In this system, efficient surface catalytic process can occur, because effective interaction of the reagents and surface is expected as the high interfacial area and the short path required for molecular diffusion in the easy identify surface [10].

To put this idea into practice, we chose Suzuki reaction catalyzed by palladium as a model reaction to evaluate and compare

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Scheme 1. The structure of cyclopalladated ferrocenylimines functionalized polymer brushes film (**Pd/PBs**).

the catalytic activity. The Suzuki reaction had been the most studied in neat water under heterogeneous palladium catalysis [11]. Meanwhile, versatile transformations using Pd catalysts usually had been developed [12]. Our team had done a lot works in past decades about the synthesis and catalysis of cyclopalladated ferrocenylimines, which were efficient catalysts for carbon–carbon coupling reactions in organic solvent or aqueous medium [13,14]. Recently, we prepared cyclopalladated arylimine functionalized polymer brushes and preliminarily discussed the catalytic activity and recyclability in heterogeneous Suzuki reaction [15]. However, the functionalized polymer brushes catalysts showed decreasing activities (lengthened reaction times) with high yield in recycle studies because of the intertwining and aggregation of long-chain octadecyl in cyclopalladated arylimine, which hindered the interactions of reactants and the active center of Pd on polymer brushes film. Therefore, rational design of suitable catalysts should be closely linked to deeper insights into mechanisms involved at a nanomolecular level.

As described above, catalytic polymer brushes film on solid substrates is suitable to study heterogeneous catalysis because they can characterize, identify, and estimate the nature of the surface species by various experimental techniques. We thus reasoned that by using a catalyst with unified, controlled, and tunable characteristics, one could detect the structural changes associated with oxidative addition more readily and more reliably to shed light on the Pd surface reaction mechanism. Herein, we attempted to graft cyclopalladated ferrocenylimines catalyst onto polymer brushes solid surfaces by covalent bond (Scheme 1). Then we evaluated the activity and recyclability of the resulting composites in Suzuki reaction and further explored the reasonable and feasible reaction mechanism of heterogeneous reaction.

2. Experimental

2.1. The synthesis of cyclopalladated ferrocenylimines functionalized polymer brushes film

The cyclopalladated ferrocenylimines functionalized polymer brushes films were prepared according to the published procedures [15]. The details about the major steps of the processing are as follows: hydrophilic treatment wafers by pirhana solution were functionalized with 3-aminopropyl triethoxysilane (2.1 mmol). Then, amino-functionalized wafers were immersed in a solution of 2-bromoisobutyryl bromide (3.3 mmol) in 25 mL of dry dichloromethane containing TEA (7.0 mmol) to react 12 h and obtained initiator-functionalized wafers. Next, initiator functionalized wafer was placed into the flask which included *N*-hydroxymethyl acrylamide (50 mmol), 2,2'-bipyridine (1.0 mmol),

CuCl (0.5 mmol), and 15 mL of the mixture (methanol/water: 4:1) proceed for 4.5 h at room temperature under nitrogen atmosphere. At last, the PHAM-grafted substrates were immersed in 40 mL of dried THF with *N,N'*-carbonyldiimidazole (12 mmol) and a solution of cyclopalladated ferrocenylimines (0.001 g) in THF 48 h to get **Pd/PBs**.

2.2. General procedure for the Suzuki reaction of aryl halide with phenylboronic acid

Aryl halide (0.125 mmol), phenylboronic acid (0.15 mmol), K_2CO_3 (0.15 mmol) and *n*-Bu₄NBr (0.15 mmol) were combined with 3 mL water in a small round-bottomed flask used for “homogeneous” and “heterogeneous” runs. The reaction mixture was stirred at 80 °C for 12 h, then, the mixture was acidified, and the product was extracted by ethyl ether for three times. The combined organic phase was dried with $MgSO_4$, filtered, and solvent was removed on a rotary evaporator. Crude product was transferred into a 10 mL volumetric flask to fix its quantity in ethyl acetate. The yields were determined by high performance liquid chromatography (HPLC), based on the peak area ratio between the products. The HPLC conditions were a Zorbax eclipse Xdb C18 column (150 × 4.6 mm 5 μm) with methanol/acetonitrile as the mobile phase, and a flow rate of 1 mL/min.

2.3. Atomic absorption spectroscopy (AAS) analysis

The amounts of cyclopalladated ferrocenylimines immobilized on solid substrates were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (ICAP 6000 Series, Thermo Scientific). The sample treatments were as follows: Pd/PBs (quartz plate or round-bottomed flask) was boiled in concentrated nitric acid, and then, residual solid was dissolved with 2 M hydrochloric acid and transferred into a 10 mL volumetric flask to fix its quantity in water.

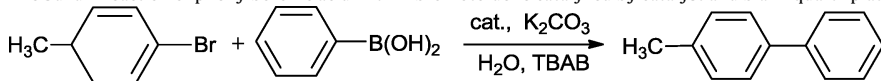
3. Results and discussion

3.1. Preparation of cyclopalladated ferrocenylimine functionalized polymer brushes film

The cyclopalladated ferrocenylimines functionalized polymer brushes film (**Pd/PBs**) grafted on silicon, glass and quartz surfaces had been synthesized as previous work [15]. The amounts of Pd in **Pd/PBs** were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The Pd content of the catalytic film on the solid slide was found to be 1.2×10^{-6} mmol cm⁻². The composition and morphology of the surfaces obtained along with the immobilization process at each step (showed in Supporting Information) were characterized by water contact angle (WCA), ultraviolet–visible spectroscopy (UV–vis), X-ray photoelectron spectroscopy (XPS), atomic force microscope (AFM), low-angle X-ray diffraction (LAXD) and cyclic voltammetry (CV). The ordered, oriented structure and unobvious layered structure in **Pd/PBs** had been demonstrated by the characterization methods. These results indicated that mostly catalysts were grafted onto the surface of polymer brushes on the solid substrates, which prompted us to explore the surface chemical reactions in heterogeneous catalysis system.

3.2. Heterogeneous catalytic properties of Pd/PBs

As mentioned above, Suzuki reaction usually served as a model for characterization of new catalysts. Heterogeneous catalysts based on different organic and inorganic supports have been reported for this versatile and powerful method of C–C bond

Table 1The Suzuki reaction of phenylboronic acid with 4-bromotoluene catalyzed by catalyst and blank quartz plate in solution^a

Entry	Catalytic system	Catalyst (10 ⁻⁶ mmol)	Time (h)	Product	Yield (%) ^b
1	Pd/PBs	7.8	12	<i>p</i> -CH ₃ -Ph-Ph	99
2	Homogeneous	1000	24	<i>p</i> -CH ₃ -Ph-Ph	90
3 ^c	Homogeneous	500	24	<i>p</i> -CH ₃ -Ph-Ph	73
4	Homogeneous	50	48	<i>p</i> -CH ₃ -Ph-Ph	Trace
5	Quartz plate	–	48	–	No reaction

^a Reaction conditions: 4-bromotoluene 0.125 mmol, PhB(OH)₂ 0.15 mmol, K₂CO₃ 0.15 mmol, TBAB(*n*-Bu₄NBr) 0.15 mmol, H₂O 3 mL, 80 °C, quartz plate (30 mm × 10 mm × 1 mm).

^b Yields determined by HPLC, based on the products.

^c PhB(OH)₂ 0.3 mmol.

formation [1,11]. The catalytic activity and recyclability of the cyclopalladated ferrocenyylimines functionalized polymer brushes film (**Pd/PBs**) were evaluated in Suzuki reaction of 4-bromotoluene with phenylboronic acid in neat water at 80 °C temperature (Table 1).

Under optimized reaction conditions [15], **Pd/PBs** displayed much higher catalytic activity even with few catalyst loading, to yield 99% 4-methylbiphenyl as the only product (as analyzed by HPLC, yield based on 4-bromotoluene and the product) compared with their analog cyclopalladated ferrocenyylimines in homogeneous, indicating that the well-ordered and higher density catalysts were more efficient for the catalytic system. These conditions were very competitive, especially compared to MNP-supported dendritic catalysts noncovalently grafted Pd complexes, which require 2.4–5 mol% of metal [16]. The difference in catalytic activity was attributed to the easy accessibility to the active sites originating from the unique films architecture, which enhanced cooperation of the active sites [8]. These conjectures would be proved by later discussions for the mechanism of the reaction process. Moreover, the catalytic activity of cyclopalladated ferrocenyylimines in homogeneous was unfavorable at the low catalyst concentration (Table 1, entry 4). The Suzuki reaction catalyzed by blank quartz plates cannot proceed under the same reaction conditions (Table 1, entry 5). When catalyst substrate was taken out from the reaction mixture after 3 h, 35% yields of product were detected. No more products could be obtained if the reaction continued to 24 h. However, when the catalyst substrate was put back into a new reaction solution, a yield of 95% products could be obtained after 12 h again. These controlled trials clearly showed that the functional catalyst films for catalyzing Suzuki reaction was in heterogeneous catalytic process. These cyclopalladated ferrocenyylimines functionalized polymer brushes film exhibited higher catalytic activity, comparing with cyclopalladated arylimine functioning polymer brushes reported in our previous results [15]. The reason may be that the substrates were more accessible to the Pd active sites of the catalyst on the polymer brushes surface. All the results obtained above implied that a heterogeneous process occurred on the catalyst surfaces.

The coupling reactions of arylboronic acids with various aryl bromides were performed in the presence of **Pd/PBs** in neat water (Table 2). Good to excellent yields of products (75–99%) were obtained (Table 2, entries 1–6), even in the case of electron-rich (R = 4-OMe: entry 2, 4-NH₂: entry 5) or bulky (entry 6) substrates. A coupling reaction of 2-bromopyridine and 1-bromonaphthalene gave the products in lower yields (40–45%) probably due to the electronic effect (entries 7 and 8). To the arylboronic acid of different substituents (entries 9–12), the yields were also excellent (80–95%). All the results above indicated that the **Pd/PBs** were efficient for Suzuki reaction in heterogeneous system.

3.3. The recyclability and stability of **Pd/PBs**

Recycling experiments were carried out by using the round-bottomed flasks in which Pd catalysts were grafted onto the internal surface for the Suzuki reaction of 4-bromotoluene and phenylboronic acid (Fig. 1). That was to say that the flasks were not only the reactors but also the catalysts, which simplified the reaction operations [14] as depicted in Scheme 2. Although a decrease of yield was observed after eight reaction cycles, yields of 4-methylbiphenyl maintained at 80% over 10 runs. These results confirmed that **Pd/PBs** was highly stable as the heterogeneous catalysts under these reaction conditions. If higher 92–94% yield was obtained after many cycles, for example, reaction time must be prolonged to 18 h after six rates. These results echoed observations by other researchers of retained high yield with decreasing activities (or lengthened reaction times) upon recycle of catalysts [8,15].

This phenomenon might be caused by the overlay on the surface of the catalyst films by reactants and products. And the inactivation of Pd active center in catalytic cycle was also one of the reasons. These reasons were indirectly confirmed by results of little catalyst decrease after eight recycles measured by ICP-AES (Fig. S8), and stable cyclic voltammograms of **Pd/PBs** modified ITO glass in recycling experiments (Fig. S9). The amount of Pd measured by ICP-AES showed that 7.17×10^{-6} mmol of Pd was detected in round-bottomed flask after two runs. With the increase of the cycle times, the amount of Pd in round-bottomed flask remained unchanged and maintained at an order of magnitude (4.87×10^{-6} mmol even after the eighth cycle). These results implied that a strong chemical bond binding on the substrates of cyclopalladated ferrocenyylimines could prevent the Pd from leaching during the catalytic process.

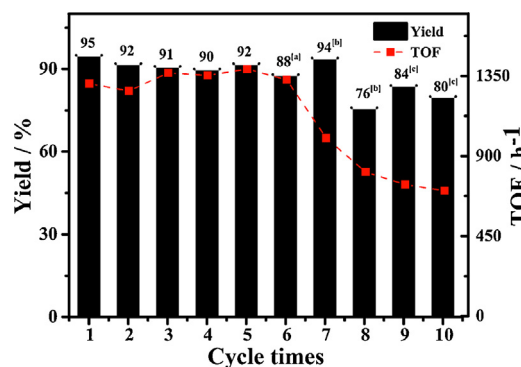
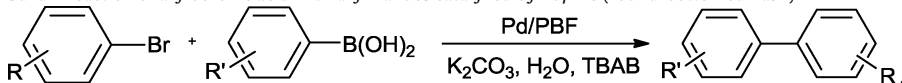


Fig. 1. Recycling experiments of the Suzuki reaction catalyzed by **Pd/PBs** (round-bottomed flask). Reaction conditions: 4-bromotoluene 0.125 mmol, PhB(OH)₂ 0.15 mmol, K₂CO₃ 0.15 mmol, *n*-Bu₄NBr 0.15 mmol, H₂O 3 mL, 80 °C, 12 h. (a) Isolated yield, (b) 18 h, and (c) 24 h.

Table 2
Suzuki reaction of arylboronic acid with aryl halides catalyzed by Pd/PBs (round-bottomed flask)^a

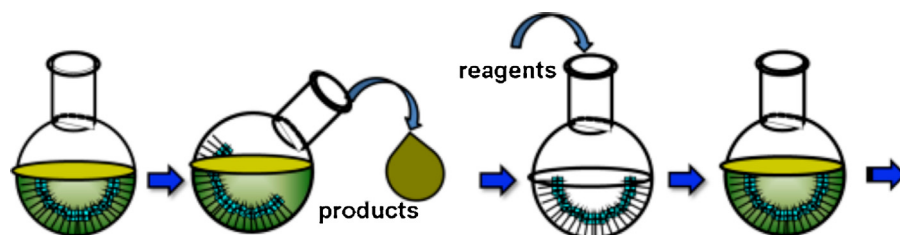


Entry	Ar-Br	Ar-B(OH) ₂	Product	Yield ^b (%)
1	<i>p</i> -NO ₂ -Ph	Ph	<i>p</i> -NO ₂ -Ph-Ph	99
2	<i>p</i> -CH ₃ O-Ph	Ph	<i>p</i> -CH ₃ O-Ph-Ph	98
3	<i>p</i> -NC-Ph	Ph	<i>p</i> -NC-Ph-Ph	88
4	<i>p</i> -F ₃ C-Ph	Ph	<i>p</i> -F ₃ C-Ph-Ph	99
5	<i>p</i> -H ₂ N-Ph	Ph	<i>p</i> -H ₂ N-Ph-Ph	93
6	1,3-dimethy-Ph	Ph	1,3-dimethy-Ph-Ph	75
7	2-bromopyridine	Ph	2-bromo-Py-Ph	40
8 ^c	1-bromon-NP	Ph	1-bromon-NP-Ph	45
9	<i>p</i> -Me-Ph	<i>p</i> -OCH ₃ -Ph	<i>p</i> -OCH ₃ -Ph-Ph-(<i>p</i> -Me)	84
10	<i>p</i> -Me-Ph	1,3-difluoro-Ph	1,3-difluoro-Ph-Ph-(<i>p</i> -)Me	91
11	<i>p</i> -Me-Ph	Pyrimidine	Pyrimidine-Ph-(<i>p</i> -)Me	80
12	<i>p</i> -Me-Ph	5-(methoxycarbonyl)-2-methyl-Ph	5-(methoxycarbonyl)-2-methyl-Ph-Ph-(<i>p</i> -)Me	95

^a Reaction conditions: phenylboronic acid 0.15 mmol, aryl halides 0.125 mmol, catalyst 7.8×10^{-6} mmol, TBAB 0.15 mmol, K₂CO₃ 0.15 mmol, H₂O 3 mL, 80 °C, 12 h, round-bottomed flask 5 mL.

^b Yield by isolated.

^c NP: naphthyl.



Scheme 2. Illustrations of the reaction operations used flask reactors linked with Pd/PBs.

It was of particular note that significantly electrochemical signal was observed in cyclic voltammograms at recycling experiments (Fig. S9). Cyclic voltammograms of the cycles showed well-defined surface waves consisting of symmetric oxidation and reduction waves except the 10th cycle. These peaks were ascribed to the redox of the ferrocene moieties (Fc/Fc⁺), showing that the cyclopalladated ferrocenylienes were still located on the electrode stably. However, the height of the peak weakened linearly as the cycle times increased up to 8 and disappeared at 10th cycle. Meantime, the reversibility of cyclic voltammetry curves also became worse along with the increase in cycle times, which indicated low electroactivity and the slow electron transfer in the catalyst films. This was presumably because that the counterion movements through the catalyst films were disturbed by the adsorption reactants, which behaved as an insulator and/or a barrier [17]. The potential separation (ΔE_p) increased after recycling experiments (Table S3). It was because that the rate of electron transfer might become slower with increasing distance between the redox site and the electrode surface [18].

3.4. Plausible heterogeneous mechanism

Researcher's explored processes in heterogeneous catalysis illustrated the importance of the interfaces with surface active centers. However, the investigations of mechanism were usually confined to the structural changes and morphology analysis before and after the catalysis [19]. The lack of detailed researches of heterogeneous catalytic process, left questions about the generality and validity of such mechanism studies. It was well known that the changes of surface during catalytic process were the key factor for elucidating catalytic mechanism. Thus, our aim was focus on insight into how the nature of actives by utilizing more realistic procedures which could capture part of the complexity inherent to

heterogeneous catalysis. Plots of conversion versus different reaction times for the Suzuki reaction of 4-bromotoluene with arylboronic acid in the presence of Pd/PBs were shown in Fig. S10.

Cyclic voltammograms method could provide electrochemical information which could evaluate the surface adsorption and the effects of different surface potential on the ITO electrode and enable us to reveal the surface catalytic process through investigating the electrochemical properties of catalysts at different reaction times. Fig. 2 showed cyclic voltammograms in 1 M HCl of the catalyst films on an ITO electrode at different catalysis times. Their electrochemical data were listed in Table S4. All voltammograms showed well-defined surface waves consisting of symmetric oxidation and reduction waves (Fc/Fc⁺). The height of the peak of Pd/PBs decreased till 6 h, showing that the ferrocene moieties were lower electroactivity due to the blocking of counterion permeation to the

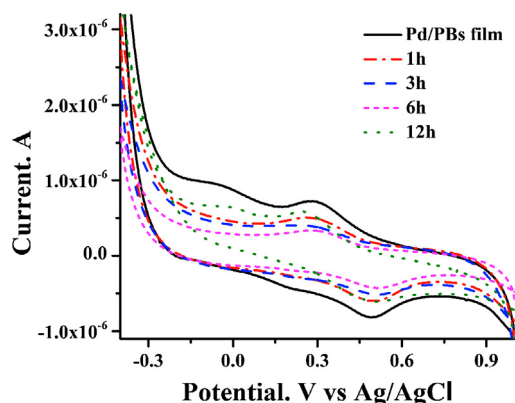


Fig. 2. Cyclic voltammograms of Pd/PBs grafted on ITO glass in Suzuki reaction at different reaction times in 1 M HCl solution at a scan rate of 10 mV/s.

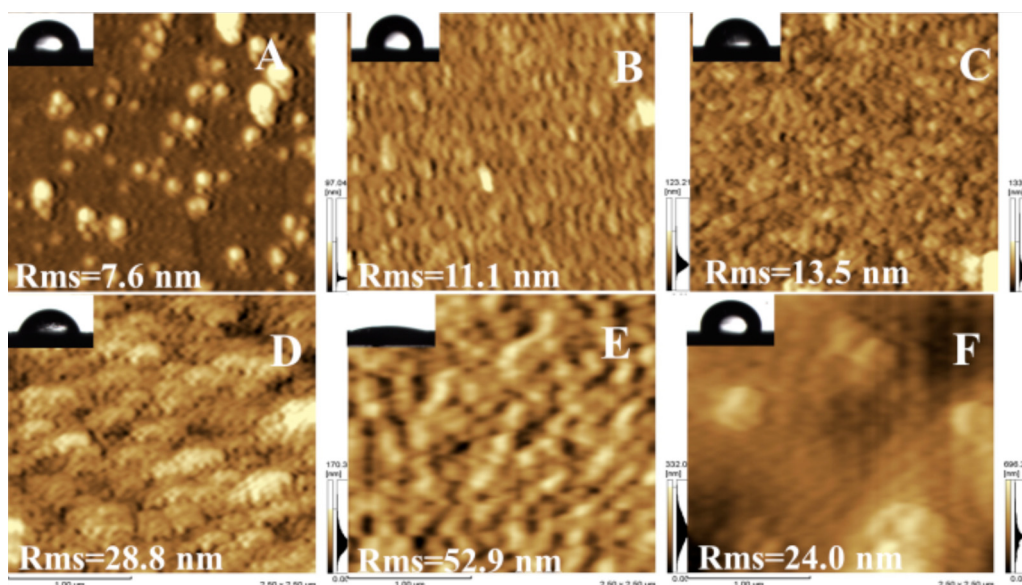


Fig. 3. AFM images of Pd/PBs in Suzuki–Miyaura reaction at (a) 0 h, (b) 0.5 h, (c) 1 h, (d) 3 h, (e) 6 h, and (f) 12 h.

redox-active sites by the reactants. It can also be explained that ferrocenyl moieties in the electrode surface were directly covered by the adsorption reactants and oxidative addition of substrates at the catalysis process. Then the peak increased when reaction was over (12 h), in which there were the reasons of the blocking of counterion permeation and the self-cleaning function of the polymer brushes [20].

Chidsey et al. [21] had reported that the ferrocene moieties in the highly ordered structure were oxidized at a more positive potential since the repulsion among the ferrocenium moieties should be larger in the well-ordered monolayer than in the less ordered monolayer. The E_{pa} of ferrocene derivatives on electrodes observed in the Pd/PBs increased along with the reaction until 525 mV and reduced to 519 mV till the end of reaction. That suggested that the ferrocene moieties in the catalytic film were ordered at the beginning of the catalysis process, which might be caused by automatically agglomerated fascicles due to the flexible structure of polymer brushes. The less ordered electrodes surfaces were observed because of the absorption of the reactant, intermediates or products in catalysis process. The potential separation (ΔE_p) increased along with reaction time (Table S4), indicating that the rate of interlayer electron transfer became slower due to increasing distance between the redox site and the electrode surface as the chains of polymer brushes. These results suggested that the process of oxidative addition of bromobenzene and phenylboronic acid, and even adsorption of base and products existed, which could influence the redox-active sites and the electrodes surface.

The corresponding analysis of AFM images and water contact angles acquired at different reaction times were precisely investigated trying to elucidate the processes proposed above (Fig. 3). As the surface rms of AFM images increased with the catalysis process, the water contact angle decreased gradually, which vividly revealed the reaction processes that occurred on the catalyst surface. It was noted that recognizable block aggregates were observed in the AFM images of Pd/PBs, which might be due to the automatically agglomerated fascicles caused by the flexible structure of polymer brushes and the adsorption in catalytic process. This agglomerated phenomenon affected the whole catalytic process, which could be observed in next step shown in Fig. 3c–e. Significant morphology changes of silicon wafer grafted with catalysts were observed during catalytic processes, with which a detailed analysis

of the catalytic processes was presented. It meant that a sequential adsorption and chemical process occurred on the catalyst film.

The morphological changes of the catalyst films during their use as catalysts were remarkable which could be illustrated by the surface changes made by the catalytically active Pd on catalyst films [22]. Studies of XPS spectra might provide more information about the dynamics of catalytically active species under reaction conditions, which could help in contributing to a better understanding of catalysis pathways [23]. These pathways had also been demonstrated by the high-resolution XPS analysis of the Pd/PBs catalysis process (Fig. 4).

The XPS analysis of the Pd in Pd/PBs clearly illustrated the cycle of Pd^{II} to Pd⁰ and Pd⁰ to Pd^{II} of the cyclopalladated ferrocenylimines on the surface of catalyst films. That was examined by the changes of palladium oxidation state during the catalysis process. As the catalyst films without reaction, Pd was detected at 343.5 and 338.3 eV BE, corresponding to the Pd 3d core level. Bromine related peaks in Br 3d spectrum appeared at 69.1 eV BE (Fig. 4C-a), which was very close to that of terminated Br of the polymer brushes chains [24]. Pd^{II} reduced to catalytically active Pd⁰ could be seen clearly in the process of the whole catalysis reaction (Fig. 4A) and oxidation of Pd⁰ to Pd^{II} in reaction with PhBr was also confirmed by XPS spectra, shown in Fig. 4C. The boron related peaks in the B 1s spectrum (Fig. 4B) Pd/PBs film at the same time also showed that coupling process occurred.

The Pd peak at 342.6 eV BE and 337.3 eV BE appeared at Pd/PBs XPS spectrum (Fig. 4A-b) at 0.5 h catalysis, which suggested that different oxidized forms of Pd were presented. These were attributed to the co-existence of species Pd^{II} and Pd^I on the surface in the Suzuki reaction. The substrates sequential adsorption and surface synergy interaction also occurred on the catalyst film, which was suggested by the boron related peaks of [PhB(OH)₂] (191.6 eV BE) in the B 1s spectrum (Fig. 4B-b) and bromine related peaks of [Pd(PhBr)_{Lx}] in Br 3d spectrum (Fig. 4C-b) reduced to 68.3 eV BE (0.8 eV smaller than Br 3d spectrum appeared at Pd/PBs without reaction).

Pd⁰ species (BE 341.1, 335.1 eV) was detected at 1 h catalysis (Fig. 4A-c) and palladium species in oxidation state (I) or (II) (BE 336.5 eV) was also found in the XPS spectrum. The bromine observed (68.1 eV BE) was compatible with that of oxidation additions (Ph-Pd-Br). Meanwhile, the intensity of boron related peaks (191.2 eV BE) increased with right-shifting of binding energy about

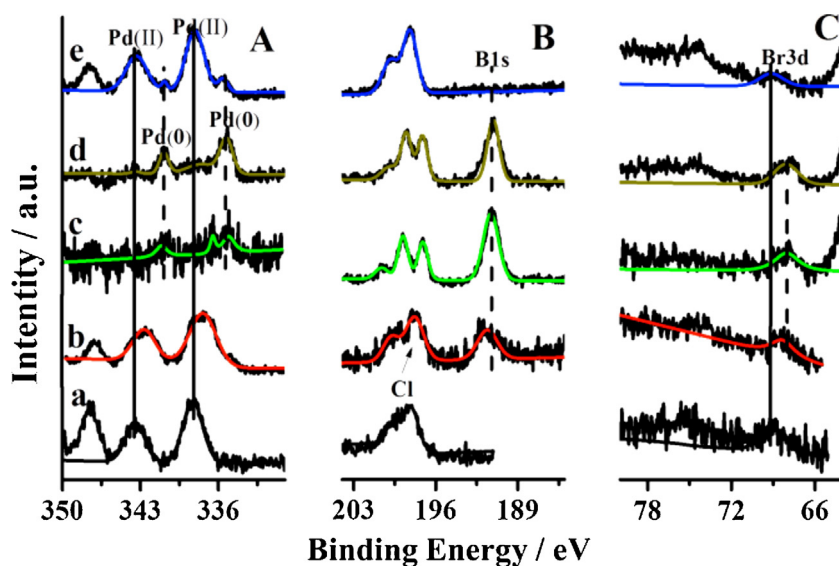


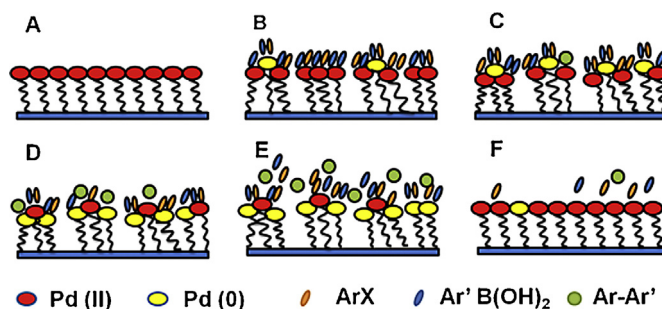
Fig. 4. High-resolution XPS spectra of Pd 3d (A), B 1s (B) and Br 3d (C) from the silicon wafer surfaces grafted Pd/PBs. (a) Before catalytic reaction, (b) after 0.5 h catalysis, (c) after 1 h catalysis, (d) after 3 h catalysis, and (e) after 12 h catalysis.

0.4 eV (Fig. 4B-c), which was the evidence that coupling process occurred. Considering the morphology of disordered closely stacked surface in AFM image (9% products yield), we thought that mixture state of the occurrences of Pd⁰ oxidation additions.

Dominating Pd⁰ (BE 340.8, 335.0 eV) and additional Pd^{II} (BE 343.4, 337.1 eV) were shown in Fig. 4A-d at 3 h catalysis. The Pd⁰ demonstrated that the oxidative addition of aryl halide and the peak at 337.1 eV was reasonably assigned to the presence of Pd-Br species. This species on the surface of the Pd/films could arise from residual bromide associated with the oxidative addition step of the catalytic process remaining on the surface of the films, which were known to be catalytically active to form Br-Pd-aryl intermediates [25]. The boron related peaks (191.2 eV BE) in the B 1s spectrum (Fig. 4B-d) and bromine (68.1 eV BE) in Br 3d spectrum (Fig. 4C-d) of Pd/PBs film at the same time also showed that oxidation additions and coupling process occurred.

As we expected, the shape of the Pd 3d core-level spectrum was changed back to its initial state after catalysis process (Fig. 4A-e). The appearance of the Pd 3d_{5/2} showed a major peak at 338.1 eV BE with a minor peak at 335.6 eV BE, and the Pd 3d_{3/2} showed a major peak at 343.4 eV BE with a minor peak at 340.8 eV BE, which were assigned as Pd^{II} (~90%) as a major species and Pd⁰ as a minor species, respectively. The XPS analysis above indicated that the integrity of the catalyst was retained when supported on solid wafers as Pd^{II} with tiny damage was suffered in the catalysis process.

A cycle of Pd^{II} to Pd⁰ and Pd⁰ to Pd^{II} on Pd/PBs could be clearly illustrated with respect to the results of CV, WAC, AFM and XPS analysis. The speculation of surface changes of Pd/PBs in different catalysis times was shown in Scheme 3. In this approach, Pd⁰ acted as an active surface in these heterogeneous system, suggesting that the Pd/PBs catalyzed coupling of aromatic halides and borophenylic acid proceeded via a mechanism of surface-catalyzed reaction as follows: first, Pd^{II} was reduced by activation of ArB(OH)₂ in situ to Pd⁰ which remained on the surface of catalyst film. Next, activated ArX reacted with Pd⁰ via oxidative addition to yield [ArPd(II)X] (still on the surface of substrates) which interacted with ArB(OH)₂ and formed intermediates. Finally, coupling product was transferred to the solution and Pd⁰ was deposited back on the support as a Pd^{II} after the catalytic process. Because of the complexity of interactions occurring simultaneously on the surface, we thought



Scheme 3. The speculation of Pd/PBs in Suzuki reaction at (A) 0 h, (B) 0.5 h, (C) 1 h, (D) 3 h, (E) 6 h, and (F) 12 h.

that the whole catalytic process was a synergy interaction between the catalyst and the substrates to give the molecular target.

4. Conclusion

In this article, a novel highly active, reusable and stable Pd/PBs was developed, in which cyclopalladated ferrocenylamines were grafted onto silicon, glass and quartz surfaces by covalent bond. The catalytic films were tested in Suzuki reaction and displayed high activity for the preparation of various biaryls at elevated temperatures in neat water without ligands, which was satisfied with the requirement of green, sustainable and economical chemistry. Moreover, Pd catalysts attached onto surface of polymer brush allows up to the same quantitative yields with lower loading than previously reported. The catalysts films presented good reusability and stability which reused at least eight times without loss in activity and only had little Pd leaching into the crude product, which could meet the specification limits in the pharmaceutical industry without requiring tedious chromatographic purification.

We also examined existing and emerging approaches to gain insights into the catalyst active phase and catalytic mechanism using water contact angle, CV, AFM and XPS methods, which offered certain opportunities to investigate working catalyst films and to identify new details about catalytic properties that were unavailable when the novel catalyst films were used. The reasonable

and feasible reaction heterogeneous mechanism in our catalysis system was proposed, in which a cycle of Pd^{II} to Pd⁰ and Pd⁰ to Pd^{II} on catalyst nano-films could be clearly illustrated with respect to the experimental results. In this approach, Pd⁰ as an active surface acted as heterogeneous catalyst, suggesting that the heterogeneous Pd/PBs catalyzed Suzuki reaction proceeded via a mechanism of surface-catalyzed reaction. The whole catalytic process was a synergy interaction between the catalyst and the substrates to give the molecular target. Such a system, in addition, offers opportunities for characterizing surface catalysis with simple and convenient way, which is crucial for detecting dynamic changes on catalytically active species and understanding catalysis pathways. Following this approach, it is possible to identify new catalyst and reaction mechanism which is very important since that it often provides a rational way to improve catalytic activity and selectivity and to be applicable to systems as an advanced functional material with applications in heterogeneous catalysis.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.molcata.2014.08.038>.

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