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ARTICLE

The Recyclable Cyclopalladated Ferrocenylimine Self-assembly Catalytic Film and Its Mechanism Investigation of Heterogeneous Catalysis

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Abstract: An efficient, reusable and stable catalyst nano-sheet film (Si-CDI-Pd) was developed, in which cyclopalladated ferrocenylimines were grafted onto silicon, glass and quartz surfaces by covalent bond. Water contact angle, Ultraviolet–visible spectroscopy (UV-Vis), X-ray Photoelectron Spectroscopy (XPS), atomic force microscope (AFM), Low-angle X-ray diffraction (LAXD) and cyclic voltammetry (CV) were used to characterize the structural and composition information of the modified surfaces. The immobilized catalyst films were tested in Suzuki-Miyaura reaction and displayed high activity for the preparation of various biaryls at elevated temperatures in neat water without ligands. It also presented good stability and reusability. It can be reused at least 8 times with little Pd leaching into the crude product (<2 ppm). The reasonable and feasible reaction mechanism of the heterogeneous Suzuki-Miyaura reaction based on the results of AFM, XPS, and CV tests of different reaction time were deeply explored, in which a cycle of Pd^{II} to Pd⁰ and Pd⁰ to Pd^{II} on the surface was clearly detected and illustrated. In this approach, Pd⁰ on the surface of nano-sheet films as an active surface to catalyze coupling reaction of aromatic halides and borophenylic acid proceeded via a mechanism of surface-catalyzed process.

Introduction

Palladium catalyzed C-C coupling reactions, including Suzuki, Heck, Sonogashira as well as other reactions, have gained a predominant place in contemporary organic chemistry in recent decades^[1]. The versatility and robustness of these processes have enabled major progress in total synthesis, materials development, medicinal chemistry and fine-chemical industries.^[2] Palladium catalysis usually allows selective reactions with high turnover numbers (TONs) and turnover frequencies (TOFs) under rather mild conditions.^[3] Most of these studies have been focused on homogeneous catalysis which provides excellent activity and selectivity. Despite its remarkable usefulness, homogeneous catalysis suffers from a number of drawbacks which lie in the removal and the reuse of the catalyst. Indeed, contamination of advanced chemical intermediates by palladium residues poses an acute issue for large-scale synthesis, especially in the pharmaceutical industry where metal contaminations are closely monitored.^[4] Moreover, economic and environmental views make palladium' recycling crucial.^[5] From these perspectives, heterogeneous catalysis seems particularly well suited since the palladium metal immobilized on a support could be easily removed by filtration leaving products virtually free of palladium residues.^[6]

The Suzuki reaction has been the most studied palladium-catalyzed reaction in neat water under heterogeneous catalysis^[7] to evaluate and compare the catalytic activity due to the excellent stability of boronic acids in aqueous media as well as the versatility of the cross-coupling toward functional groups. A variety of supports appropriately functionalized for a high affinity with a palladium catalyst have been proposed. Palladium supported on organic supports (polyaniline, PS-PEG, polymeric imidazole, poly-vinylpyrrolidone, chitosan, etc.)^[8], hybrid organic-inorganic Supports (Pd/SiO₂, Pd/PMO, Pd/SBA-15, silica, zeolite and metal oxide-Supported Ionic liquids, etc.)^[9] and inorganic Supports (Pd/C, metal oxides, sepiolite, hydroxyapatite, hydrotalcite, mesoporous silica, etc.)^[10] had been applied to the cross-coupling reaction. However, 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.^[11] The mechanistic studies are certainly one of the most striking weaknesses of current studies in heterogeneous catalysis^[12]. It can be anticipated that much help in improving the catalytic systems will come from a careful examination of the heterogeneous mechanism.

The primary mechanism of the coupling reactions catalyzed by solid-supported Pd was accepted that Pd catalysts catalyze in a homogeneous way by leaching Pd species^[13], which can re-deposit when the reaction comes to an end. Rapid development of sophisticated experimental techniques and theoretical modelling^[14] in recent years had allowed unprecedented insight

into the molecular nature of very complex reaction taking place on the catalyst surface as well as leaching Pd species.^[15] For example, Crudden and MacQuarrie demonstrated the thermally controlled redistribution and dissolution of palladium on the surface of Pd foil during the Suzuki reaction.^[16] There were considerable circumstantial evidences that in the latter materials, surface sites might play a direct role in the catalytic cycle.^[17] Both Ellis^[18] and Shao^[19] showed the evidences for the surface-catalyzed Suzuki–Miyaura reaction over palladium nanoparticles. The most compelling evidence for surface-driven Suzuki coupling derives from an ingenious experiment in which Davis and co-workers used a palladium nanoparticle coated AFM probe to initiate spatially controlled coupling over surface-tethered aryl halides or styrene.^[20]

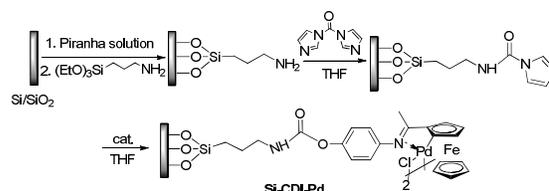
Nonetheless, despite many microscopic and kinetic studies had been carried out, unequivocal evidences for surface-catalyzed cross-coupling chemistry remained elusive. Clearly, the study of palladium based coupling reactions would get continue and potential breakthroughs in the elucidation of the dynamics of palladium and the determination of the type(s) of palladium species which were truly catalytically active. That will aid in the rational design of future generations of catalysts. Therefore, discovery of novel supports and development of suitably sensitive analytical methods will be a key point in the context of research priority. Thin films^[21] (Langmuir-Blodgett (LB) Films, Self-assemble Films, etc.) on solid slides can be characterized, identified, and estimated the nature of the surface species by variety of experimental technique. That enables thin films to be an ideal model system to study surface and interface behaviour, with which we can deeper insight into catalytic behaviour and mechanisms at a nanomolecular level.

Our recently works found that molecule orientation and morphology of cyclopalladated ferrocenyliimine in LB films could affect the catalysis efficiency in the heterogeneous Suzuki-Miyaura reaction, which clearly demonstrated that ordered structures have a major influence on a catalytic reaction.^[22] However, the LB films had desorbed from solid slides to some extent when it was placed in organic solvents or under heating conditions, which affected the experiment results. Then cyclopalladated arylimine self-Assemble films were synthesized to overcome these disadvantages.^[23] Indeed, Pd catalysts immobilized on solid slides exhibited improved catalytic activity and stability. Nevertheless, the structure of the Pd catalysts in film was not clear, which make it difficult to discuss catalytic mechanism. So, rational design of suitably catalysts should be closely linked to deeper insights into mechanisms involved at a nanomolecular level. We thus reasoned that 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 ferrocenyliimines catalyst onto solid surfaces by covalent bond and evaluate the activity and recyclability of the resulting composites in Suzuki-Miyaura reaction. By characterizing, identifying, and estimating the nature of the surface species, we will provide

strong evidences that the heterogeneous Suzuki-Miyaura reaction catalyzed by catalyst nano-sheet film was proved to be surface catalytic process.

Results and discussion

Preparation of catalyst nano-sheet films (Si-CDI-Pd)



Scheme 1. Preparation of cyclopalladated ferrocenyliimine nano-sheet films (Si-CDI-Pd).

Preparation of cyclopalladated ferrocenyliimines nano-sheet films which grafted onto silicon, glass and quartz surfaces was illustrated in Scheme 1. The wafers were hydrophilic treated by piranha solution first and were functionalized with (3-aminopropyl) triethoxysilane. Then, amino-functionalized wafers were immersed in a THF solution of N, N'-Carbonyldiimidazole (CDI) to yield CDI-functionalized wafers which were washed and then immersed in a THF solution of cyclopalladated ferrocenyliimines for 48h to get Si-CDI-Pd.

The amounts of Pd in Si-CDI-Pd were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The Pd content of the catalyst was found to be $\sim 1.0 \times 10^{-6}$ mmol cm^{-2} in the solid slides. The composition and morphology of the surfaces obtained along with the immobilization process at each step were characterized by water contact angle, UV-Vis, XPS, AFM and CV.

Water contact angle can reflect surfaces wettability which was caused by either a chemical gradient or a gradient in topographical surface structure.^[24] Water contact angles on modified solid surfaces were shown in Figure 1.

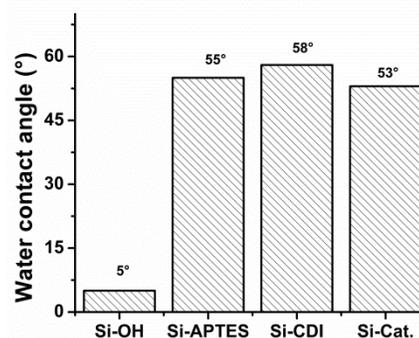


Figure 1. Water contact angles on modified solid surfaces. Si-OH (hydrophilic silicon wafers), Si-APTES (silicon wafers treated by 3-aminopropyl triethoxysilane), Si-CDI (silicon wafers modified by carbonyldiimidazole), Si-Cat. (silicon wafers linked by cyclopalladated ferrocenyliimines)

After the pre-treatment with “piranha” solution, the silicon and quartz substrate became strongly hydrophilic because it had extremely low water contact angle (5°), then gave rise to the water contact angles to 55° after APTES treatment. The water contact angles of modified solid surfaces of Si-CDI-Pd changed from 58° for modified by CDI to 53° for grafted cyclopalladated ferrocenyliimines. The changes of water contact

angles of modified solid surfaces indicated that the surface configuration had significantly changed, which could clearly reflect the chemical gradient of each step. It also meant that the catalyst films on solid substrates were obtained by self-assembly method. UV-vis absorption spectra of modified quartz plates along with the immobilization process offered further evidences of the synthesis of **Si-CDI-Pd** (Figure S1).

In order to understand more detailed information of the catalyst structure, composition, the influence of the supporting substrate with the prospect of obtaining even more efficient catalysis, AFM images (Figures 2) and XPS spectra (Figure 3) were measured at different steps of the surface derivatization process of **Si-CDI-Pd**.

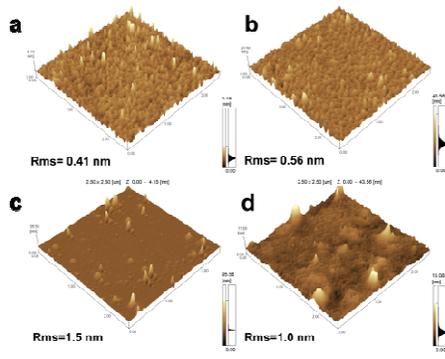


Figure 2 AFM images of the silicon wafers at immobilization process. a) hydrophilic treatment, b) treated by 3-aminopropyl triethoxysilane, c) modified by carbonyldiimidazole, d) linked by cyclopalladated ferrocenylimines.

The XPS spectra covered the Br3d, Si2p, Cl2p, C1s, N1s, Fe2p3 and Pd3d5 energy ranges. The O1s core level was not shown here because it gave no useful information. The obtained XPS of clean silicon wafer only gave two Si2p peaks (99.1 eV BE, 103.0 eV BE) attributed to the bulk elemental Si and silicon oxide was not displayed also. The binding energies (BEs) obtained for all core-level spectra presented here were summarized in Table S1.

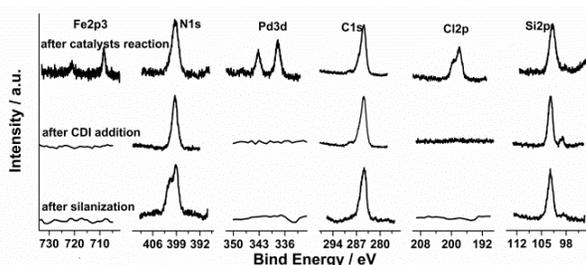


Figure 3 High-resolution XPS spectra of the Pd3d5, C1s, Fe2p3, N1s, Cl1s, and Si2p of silicon surface at different steps of surface modification.

The composition and morphology of the silicon wafers immobilization process of **Si-CDI-Pd** were shown below. The AFM images acquired on clean wafer (Figure 2a) revealed a flat and evenly aligned surface with 0.41nm rms. And then a smooth and homogeneous surface with a ca. 0.56 nm rms images (Figure 2b) had been observed after silanization. The binding energies of C1s, N1s, and Si2p were contribution at about 228.4 eV, 399.1 eV, 99.1 eV and 102.6 eV respectively at this step. Although no new element had been detected in spectrum (Figure 3) except a shoulder spectrum 289.1 eV BE of

C1s, The AFM images obtained after CDI addition (Figure 2c) exhibited a higher rms than that observed after silanization (1.5 nm), which indicated that CDI could be introduced. High resolution XPS narrow scan for Pd3d level showed 3d_{3/2} and 3d_{5/2} at 343.2eV and 337.9eV, Cl2p level at 198.0eV and Fe2p at 708.4 eV BE, which indicated that the cyclopalladated ferrocenyliimine was attached (Figure 3). AFM investigation of the catalyst-grafted surface (Figure 2d) presented the evidence of high-density arrays and orderly structure regardless of few clusters, resulting in a lower rms of the surface rms down to 1.0 nm.

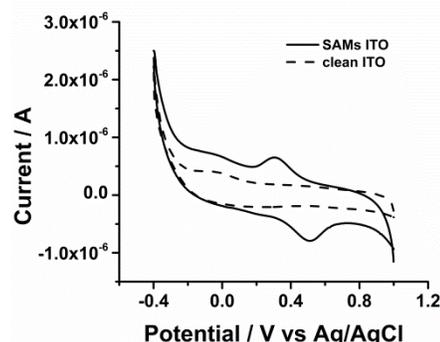


Figure 4. Cyclic voltammograms of **Si-CDI-Pd** on ITO glass (solid and dash dot line) and hydrophilicity treated ITO glass (dotted line).

Electrochemical measurements of **Si-CDI-Pd** on ITO electrodes were carried out in conventional three-electrode configuration using a saturated calomel electrode as the reference electrode and Ag/AgCl as the counter electrode. Figure 4 showed cyclic voltammograms of catalyst films on an ITO electrode in 1 M HCl solutions at scan rates of 10 mV s⁻¹. The cyclic voltammograms of cyclopalladated ferrocenylimines in THF solution was shown in Figure S2. All the potential values were listed in Table S2. The voltammograms showed well-defined surface waves consisting of symmetric oxidation and reduction waves. These peaks were ascribed to the Fc/Fc⁺ redox process in thin films, showing that the cyclopalladated ferrocenylimines were located on the electrode.

The potential separation ($\Delta E_p = E_{pa} - E_{pc}$) between the anodic and cathodic peaks of the **Si-CDI-Pd** were smaller than that obtained for catalysts in solution (Table S2), indicating that the rate of electron transfer from the catalyst films to the electrode was related structure of cyclopalladated ferrocenylimines films grafted on glass electrodes. The low electroactivity of catalyst films would be due to the blocking of counterion permeation to the redox-active sites by the highly oriented ferrocene moieties. Furthermore, the films were stable against peeling off during the potential scans since almost no variations in the cyclic voltammograms were observed after repeated successive potential scans^[25].

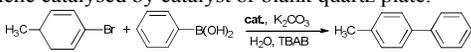
Unobvious layered structures of fabricated films proved by low-angle X-ray diffraction (LAXD) spectrum indicated that mostly catalysts were grafted onto the surface of the solid substrate. (Figure S3) CV and AFM investigation of the catalyst-grafted surface presented the evidences of high-density arrays and orderly structure. The order structure and the stability of catalyst in **Si-CDI-Pd** demonstrated by these measurements may influence the catalysis performance of

nano-sheet film, which prompted us to explore the surface chemical reactions in heterogeneous catalysis system.

Heterogeneous Catalytic Properties of Si-CDI-Pd

As mentioned above, Suzuki cross-coupling reaction usually serves as a model for characterization of new catalysts and optimization of reaction condition. Heterogeneous catalysts based on different organic and inorganic supports have been reported for this versatile and powerful method of C-C bond formation [2]. To our knowledge, only a few examples of self-assemble film catalysts had been reported but all of them were higher catalyst loading. [11]

Table 1. The Suzuki-Miyaura reaction of phenylboronic acid with 4-bromotoluene catalysed by catalyst or blank quartz plate. [a]



Entry	Catalytic system	Catalyst/ 10 ⁻⁶ mmol	Time/ h	Product	Yield ^[b] (%)	TON
1	Si-CDI-Pd	7.6	12	p-CH3-Ph-Ph	99	16283
2	Homogeneous	1000	24	p-CH3-Ph-Ph	90	113
3 ^[c]	Homogeneous	500	24	p-CH3-Ph-Ph	73	182
4	Homogeneous	50	48	p-CH3-Ph-Ph	Trace	-
5	quartz plate	-	48	p-CH3-Ph-Ph	No reaction	-

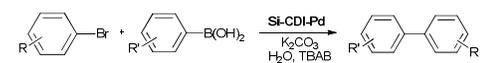
[a] Reaction conditions: 4-bromotoluene 0.125 mmol, PhB(OH)₂ 0.15 mmol, K₂CO₃ 0.15 mmol, n-Bu₄NBr(TBAB) 0.15 mmol, H₂O 3 mL, 80 °C, 12h. Quartz plate (30× mm×10 mm×1 mm). [b] Yields determined by HPLC, based on the products. [c] PhB(OH)₂ 0.3 mmol.

The catalytic activity of Si-CDI-Pd was evaluated in Suzuki-Miyaura reaction (Table 1). The catalytic activity of cyclopalladated ferrocenylimines in homogeneous was unfavourable at the low catalyst concentration (Table 1, entry 4). The Suzuki-Miyaura reactions catalyzed by blank quartz plates cannot proceed under the same reaction conditions (Table 1, entry 5). Controlled trials (Supporting information) clearly showed that it was a heterogeneous catalytic process. Si-CDI-Pd displayed much higher catalytic activity even with few catalysts loading, in which yield 99% 4-methylbiphenyl as the only product compared with their analogy cyclopalladated ferrocenylimines 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 [13]. There were clear advantages on fixing the orientation of a catalyst in terms of its ability to influence the activity and selectivity.

The coupling reactions of arylboronic acids with various aryl bromides were performed in the presence of catalyst films (Table 2). Good to excellent yields of products (71–99%) were obtained (Table 2, entry 1-6), even in the cases of electron-rich (R=4-OMe: entry 2, 4-NH₂: entry 5) or bulky (entry 6) substrates. A coupling reaction of o-substituted aryl bromides gave the products in lower yields probably due to the electronic effect (entries 7 and 8). For arylboronic acid, the conversion were excellent (entries 9-12), except pyrimidine obtained moderate yield (64%, entry 11), indicating that Si-CDI-Pd was efficient for Suzuki-Miyaura reaction in heterogeneous system. These conditions used above were also competitive in terms of

ligand and solvent [17]. For each substrate, no ligands conferred about the higher activity to Pd in neat water.

Table 2. Suzuki reaction of arylboronic acid with aryl halides catalysed by Si-CDI-Pd (Round-bottomed flask) [a]



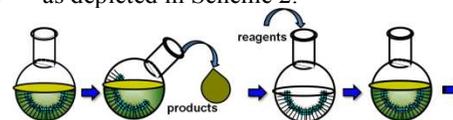
Entry	Ar-Br	Ar-B(OH) ₂	Product	Yield ^[b] (%)
1	<i>p</i> -NO ₂ -Ph	Ph	<i>p</i> -NO ₂ -Ph-Ph	99
2	<i>p</i> -CH ₃ O-Ph	Ph	<i>p</i> -CH ₃ O-Ph-Ph	97
3	<i>p</i> -NC-Ph	Ph	<i>p</i> -NC-Ph-Ph	98
4	<i>p</i> -F ₃ C-Ph	Ph	<i>p</i> -F ₃ C-Ph-Ph	71
5	<i>p</i> -H ₂ N-Ph	Ph	<i>p</i> -H ₂ N-Ph-Ph	97
6	1,3-dimethyl-Ph	Ph	1,3-dimethyl-Ph-Ph	80
7	2-bromo pyridine	Ph	2-bromo-Py-Ph	60
8 ^[c]	1-bromon-NP	Ph	1-bromon-NP-Ph	34
9	<i>p</i> -Me-Ph	<i>p</i> -OCH ₃ -Ph	<i>p</i> -OCH ₃ -Ph-Ph-(<i>p</i> -Me)	85
10	<i>p</i> -Me-Ph	1,3-difluoro-Ph	1,3-difluoro-Ph-Ph-(<i>p</i> -Me)	99
11	<i>p</i> -Me-Ph	Pyrimidine	Pyrimidine-Ph-(<i>p</i> -Me)	64
12	<i>p</i> -Me-Ph	5-(methoxycarbonyl)-2-methyl-Ph	5-(methoxycarbonyl)-2-methyl-Ph-Ph-(<i>p</i> -Me)	96

[a] Reaction conditions: phenylboronic acid 0.15 mmol, aryl halides 0.125 mmol, catalyst, 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.

Nevertheless, there are few discussions about whether surface could influence the catalytic properties in reported Suzuki reaction involving SAMs [21] or not [15], which was an important factor for heterogeneous catalytic system. The absence of a negative effect of surface might be due to the presence of the orderly arrangement interface, which could enhance the performance of the coupling by creating favourable interactions with aryl substrates. [23]

The recyclability and stability of Si-CDI-Pd

Recycling experiments were carried out by using the round bottom flasks in which Pd catalysts were grafted onto the internal surface. That is to say that the flasks are not only the reactors but the catalysts, which simplified the reaction operations [23] as depicted in Scheme 2.



Scheme 2. Illustrations of the reaction operations used flask reactors.

In the case of Si-CDI-Pd, although decreased yield was observed after eight reaction cycles, moderate yield was still obtained after tenth cycle. There was no catalyst deterioration had been observed, confirming the high recyclability and stability of the heterogeneous catalysts (Figure 5b). ICP-AES

measurement showed trace amounts Pd-leaching during the recycling process (Table S4). However, The reaction time must be prolonged to 18 hours after six cycle. The similar observation were presented by other researchers of retained high yield with decreasing activities (or lengthened reaction time) upon recycle of catalysts^[26]. We speculated that it could be caused by the overlay on the surface of the catalyst films by reactants and products, or the inactivation of Pd active center in catalytic process, which could be further proved by the CV tests (Figure S4).

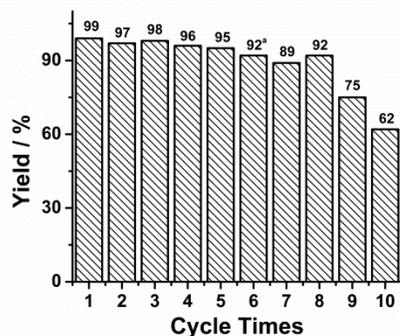


Figure 5. Recycling experiments of the Suzuki-Miyaura reaction catalyzed by Si-CDI-Pd.

Plausible heterogeneous mechanism

Researchers have used surface science methods^[27] and metal single crystals^[28] to explore elementary processes in heterogeneous catalysis, in which illustrated the importance of the interfaces with surface active centers to reveal the reaction mechanism at these active sites. However, the investigations of mechanism were usually confined to the structural changes and morphology analysis before and after the catalysis.^[19, 23] The lack of detailed researches of heterogeneous catalytic process leave questions about the generality and validity of such mechanism studies. It was well known that the changes of surface during catalytic process are the key factor for elucidating catalytic mechanism. Thus, our aim is focused on insight into what the nature of actives is by utilizing more realistic procedures which could capture part of the complexity inherent to heterogeneous catalysis.

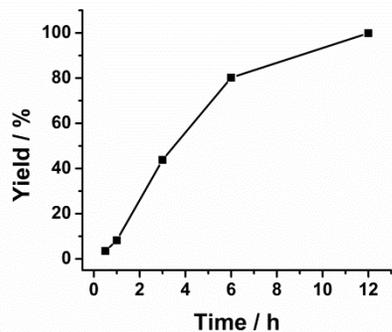


Figure 6. Isolated yield of Suzuki-Miyaura reaction catalyzed by Si-CDI-Pd at different reaction time.

Plots of conversion versus reaction time for the Suzuki reaction was shown in Figure 6. Quantitative conversions were obtained within 12 hours. The corresponding analysis of CV (Figure S5), AFM images and water contact angles acquired at

different reaction time were precisely investigated (Figure 7). 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.

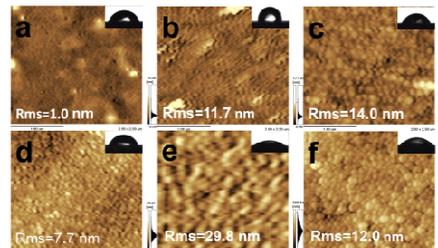


Figure 7. AFM images of Si-CDI-Pd at different reaction time in Suzuki-Miyaura reaction. a) 0 h, b) 0.5 h, c) 1 h, d) 3 h, e) 6 h, f) 12 h. Insets were water contact angles.

Figure 7a showed smooth, order and uniform surface morphologies of the catalyst films with low rms (1.0 nm), in which the water contact angles were 55°. However, considerable restructuring of the catalyst surfaces were observed during reaction. Figures 7b-e was the surface morphologies of Si-CDI-Pd at different reaction time, in which remarkable morphological changes of catalyst film were detected. These changes indicated the occurrence of catalytic processes. It meant that a sequential adsorption and connecting process occurred on the catalyst film. The confused aggregation phenomenon on the catalyst film surface with higher rms (29.8 nm) appeared (Figure 7e) at 6 hour catalysis, which revealed that the drastic catalytic process happened. Uniform, homogeneous and order pattern reappeared in Figure 7f when the catalytic reaction was completed. These results indicated that Si-CDI-Pd as heterogeneous catalyst catalyzed coupling of aromatic halides and borophenylic acid proceeded via surface-catalyzed process.

The morphological changes of the catalyst films were remarkable, which could be illustrated by the surface changes made by the catalytic reaction.^[29] There was an interaction between the reactants and the support catalyst films which was consistent with previous studies that PdNP high reactivity resulted in surface changes on PdNPs and supporting H-CNTs during the Suzuki reaction.^[18] Significant morphology changes of solid slices grafted with catalysts were observed during catalytic processes, in which could be illustrated by the surface changes made by the catalytical active Pd on catalyst films.^[27] The speculation of surface morphology changes of Si-CDI-Pd in different catalysis times based on AFM images and water contact angles were precisely investigated trying to elucidate the processes proposed (Figure 8a).

Studies of XPS spectra may provide more information about the dynamics of catalytic active species under reaction conditions, which may contribute to a better understanding of catalysis pathways. Analysis of the surfaces of the different samples using XPS was carried out to determine what the relationship was between the chemical changes and the obvious morphological changes accompanied in the catalyst films.

The XPS analysis of the palladium illustrated the cycle of Pd^{II} to Pd⁰ and Pd⁰ to Pd^{II} of the cyclopalladated ferrocenylimines on the surface of Si-CDI-Pd (Figure 8b). It

was examined by the changes of palladium oxidation state during the catalysis process. Pd^{II} in **Si-CDI-Pd** before reaction was detected at 343.5 and 338.3 eV BE corresponding to the Pd 3d core level. Reduced Pd^{II} to catalytic active Pd⁰ could be seen in the whole process of catalysis reaction and oxidation state of Pd⁰ to Pd^{II} in reaction with PhBr was also confirmed by XPS spectra.

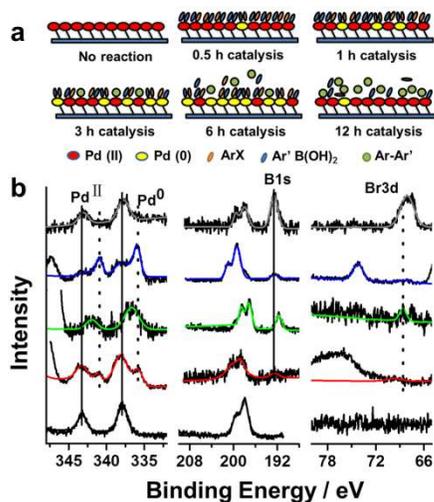


Figure 8. a) The speculation of **Si-CDI-Pd** at different catalysis times in Suzuki-Miyaura reaction. b) High-resolution XPS spectra of Pd3d, B1s and Br3d of **Si-CDI-Pd** at 0 h (black), 0.5 h (red), 1 h (green), 6 h (blue) and 12 h (gray).

Pd⁰ (BE 335.8, 341.1 eV) was found in the XPS spectrum of **Si-CDI-Pd** after 0.5 h catalysis, indicating that the formation of active Pd⁰ was considered at the beginning of catalytic cycle. The decrease of Pd^{II} (BE 343.3, 338.1 eV) intensity was found to give the direct evidences of reduction of Pd^{II} to Pd⁰ in the presence of phenylboronic acid in Suzuki reactions^[30] The broadening FWHM of the Pd^{II} peak (1.98 eV BE and 1.79 eV BE) suggested that different oxidized forms of palladium were presented^[23]. Boron related peaks (192.5 eV BE) in the B1s spectrum and bromine in Br3d spectrum (70.0 eV BE) suggested that substrates sequential adsorption and surface synergy interaction occurred on the catalyst film.

The Pd peak at 342.1 eV BE and 336.8 eV BE appeared at XPS spectrum after 1 h catalysis, which was attributed to the co-existence of Pd⁰ species and Pd^{II} species (even if Pd^I^[31]). That could be explained as a result of incomplete reduction of Pd^{II} to Pd⁰ or Pd⁰ oxidation additions on the surface. Meanwhile, the boron related peak (191.7 eV BE) and bromine observed (68.6 eV BE) which are assigned to the oxidative additions (Pd(PhBr)L_x)^[32], presented the occurrences of oxidative additions in catalytic process.

Main Pd⁰ (BE 340.5, 335.2 eV) and minor Pd^{II} (BE 343.2, 337.6 eV) were showed in Figure 2d. The major of Pd⁰ demonstrated the evidences that the oxidative addition of aryl halide to Pd⁰ (in the surface) was a key stage of the Suzuki reaction as well as other reactions catalysed by palladium with aryl halides as substrates. The minor peak at 337.6 eV BE was reasonably assigned to the presence of Pd-Br species or intermediate of [Bu₄N]₂[PdBr₄]. This species on the surface might arise from residual bromide of the catalytic process, which were known to be catalytically active to form Br-Pd-aryl intermediates^[33]. The bromine in Br3d spectrum reduced to 68.3 eV BE which was very close to that found of

[Pd(PhBr)L_x] also presented the continuous oxidative additions in catalytic process.

As we expected, the shape of the Pd3d core-level spectrum was changed back to its initial state (343.1 eV BE and 337.8 eV BE). It indicated that the integrity of the catalyst was retained as Pd^{II} with little damage suffered in the catalysis process.^[34]

A cycle of Pd^{II} to Pd⁰ and Pd⁰ to Pd^{II} on the surface of **Si-CDI-Pd** could be clearly illustrated with respect to the results of CA, AFM and XPS analysis. In this approach, **Si-CDI-Pd** as heterogeneous catalyst catalyzed coupling of aromatic halides and borophenyl acid proceeded via a mechanism of surface-catalyzed reaction as follow: First, Pd^{II} was reduced by activation of ArB(OH)₂ in situ to Pd⁰ on the surface of catalysts film. Next, activated Ar⁺X reacted with Pd⁰ via oxidative addition to yield [Ar⁺Pd^{II}X] (still on the surface) which interacted with ArB(OH)₂ in the synergy way to form intermediates. Finally, coupling product was transferred to the solution and Pd⁰ was deposited back on the support as Pd^{II} after the catalytic process. Because of the complexity of interactions occurring simultaneously on the surface, we thought that the whole catalytic process was a synergy interaction between the catalyst and the substrates to give the target molecular.

Conclusions

In this article, an efficient, reusable and stable Pd nano-sheet film was developed by immobilized cyclopalladated ferrocenylimines onto solid slice. The order, orientation structure catalysts in **Si-CDI-Pd** were demonstrated by AFM measurements. **Si-CDI-Pd** was tested in Suzuki-Miyaura reaction and displayed higher catalytic activity even with few catalysts loading^[35] for the preparation of various biaryls at elevated temperatures in neat water without ligands. There were clear advantages on fixing the orientation of a catalyst in terms of its ability to influence the activity and selectivity.

Moreover, **Si-CDI-Pd** enabled the facile reaction and recovery of the catalyst by simply remove and wash, which was satisfied with the requirement of green, sustainable and economical chemistry. Good stability and reusability were presented that it was reused at least 8 times with little Pd leaching into the crude product, which could meet the specification limits in the pharmaceutical industry without requiring tedious chromatographic purification.

The reasonable and feasible reaction mechanism based on the results of different reaction time was deeply explored. **Si-CDI-Pd** acted as heterogeneous catalyst to catalyse Suzuki-Miyaura reaction carried through surface-catalysis process. The cycle of Pd^{II} to Pd⁰ and Pd⁰ to Pd^{II} on the surface was clearly detected and illustrated. It also demonstrated the evidences that the oxidative addition of aryl halide to Pd⁰ (in the surface) was a key stage of the Suzuki reaction as well as other reactions catalysed by palladium catalysts. 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 importance since that it often provides a rational way to improve catalytic activity and selectivity.

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Notes and references

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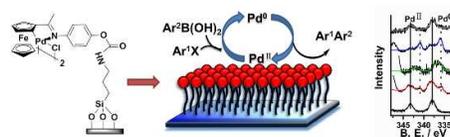
- Cross-Coupling Reactions. A Practical Guide, (Ed.: N. Miyaura), Topics in Current Chemistry, Springer Verlag, Berlin, 2002; Metal Catalyzed Cross-Coupling Reactions, / (Eds.: A. de Meijere, F. Diederich), 2nd edn. Wiley-VCH, Weinheim, 2004; S. L. Buchwald, *Acc. Chem. Res.*, 2008, **41**, 1439.
- C. Torbora and M. Beller*, *Adv. Synth. Catal.*, 2009, **351**, 3027; G. Zeni, R. C. Larock, *Chem. Rev.*, 2006, **106**, 4644; D. Wang, D. Denux, J. Ruiz and D. Astruc*, *Adv. Synth. Catal.*, 2013, **355**, 129; V. Farina, *Adv. Synth. Catal.*, 2004, **364**, 1553; X.F. Wu, P. Anbarasan, H. Neumann and M. Beller*, *Angew. Chem. Int. Ed.*, 2010, **49**, 9047.
- J-C. Hierso, M. Beaupérin and P. Meunier, *Eur. J. Inorg. Chem.*, 2007, **24**, 3767.
- M. Butters, D. Catterick, A. Craig, A. Curzons, D. Dale, A. Gillmore, S. P. Green, I. Marziano, J-P. Sherlock, W. White, *Chem. Rev.*, 2006, **106**, 3002; J. Magano, J.R. Dunetz, *Chem. Rev.*, 2011, **111**, 2177–2250.
- J. A. Gladysz, *Pure Appl. Chem.*, 2001, **73**, 1319; A. Fukuoka, P.L. Dhepe, *The Chemical Record*, 2009, **9**, 224.
- Á. Molnár, *Chem. Rev.*, 2011, **111**, 2251; A. Dhakshinamoorthy, M. Opanasenko, J. Čejka, H. Garcia, *Adv. Synth. Catal.*, 2013, **355**, 247;
- M. Lamblin, L. Nassar-Hardy, J-C. Hierso, E. Fouquet, F-X Felpin, *Adv. Synth. Catal.*, 2010, **352**, 33. B. Yuan, Y. Pan, Y. Li, B. Yin, H. Jiang, *Angew. Chem. Int. Ed.*, 2010, **49**, 4054; S. Ogasawara, S. Kato, *J. Am. Chem. Soc.*, 2010, **132**, 4608; J. Wei, J. Jiao, J. Feng, J. Lv, X. Zhang, X. Shi, Z. Chen, *J. Org. Chem.*, 2009, **74**, 6283; R. Franzén, Y.J. Xu, *Can. J. Chem.*, 2005, **83**, 266.
- for Polyaniline: P Boomi, H G Prabu, J Mathiyarasu. *Eur J Med Chem.* 2014, **72**, 18. for Polymeric Imidazole: Y M Yamada, S M Sarkar, Y Uozumi, *J Am Chem Soc.* 2012, **134**, 3190. for Poly(vinylpyrrolidone): Y. Li, E. Boone, M A. El-Sayed, *Langmuir*, 2002, **18**, 4921. for Chitosan: J. J. E. Hardy, S. Hubert, D. J Macquarrie, A. J Wilson. *Green Chem.*, 2004, **6**, 53.
- for Pd/SiO₂: M. Kim, J. C. Park, A. Kim, K. H. Park, H. Song, *Langmuir*, 2012, **28**, 6441; for Pd/PMO: B. Karimi, D. Elhamifar, J. H. Clark, A. J. Hunt, *Org. Biomol. Chem.*, 2011, **9**, 7420; for Pd/SBA-15: J. Zhi, D. Song, Z. Li, X. Lei, A. Hu, *Chem. Commun.*, 2011, **47**, 10707; for Silica: Z. Chen, Z-M. Cui, F. Niu, L. Jiang, W-G Song, *Chem. Commun.*, 2010, **46**, 6524
- for Pd/C: H. Sakurai, T. Tsukuda, T. Hirao, *J. Org. Chem.*, 2002, **67**, 2721; for Metal Oxides: P. D. Stevens, G. Li, J. Fan, M. Yen, Y. Gao, *Chem. Commun.*, 2005, 4435. for Sepiolite: K. Shimizu, R. Maruyama, S. Komai, T. Kodama, Y. Kitayama, *J. Catal.*, 2004, **227**, 202, for Hydroxyapatite: R. M. Mohamed, E. S. Baeissa, *Appl. Catal. A: Gen.*, 2013, **464**, 218; for Hydrotalcite: M. Mora, C. Jiménez-Sanchidrián, J. R. Ruiz, *J. Mol. Catal. Chem.*, 2008, **285**, 79; for Mesoporous Silica: W. Fang, J. Yang, J. Gong, *Adv Func Mater*, 2012, **22**, 842.
- L. Jin, J. Liebscher, *Chem. Rev.*, 2007, **107**, 133.
- N. T. S. Phan, Matthew V.D. Sluys, C.W. Jones, *Adv. Synth. Catal.*, 2006, **348**, 609.
- J-S. Chen, A. N. Vasiliev, A. P. Panarello, J. G. Khinast, *Appl. Catal. A: Gen.*, 2007, **325**, 76; Z. Niu, Q. Peng, Z. Zhuang, W. He, Y. Li, *Chem. Eur. J.*, 2012, **18**, 9813.
- L.Xue and Z. Lin, *Chem. Soc. Rev.* 2010, **39**, 1692.
- M. Pérez-Lorenzo, *J. Phys. Chem. Lett.* 2012, **3**, 167.
- S. MacQuarrie, J. H. Horton, J. Barnes, K. McEleney, H-P. Looock, C. M. Crudden, *Angew. Chem.* 2008, **120**, 3324; *Angew. Chem. Int. Ed.* 2008, **47**, 3279.
- B. M. Choudary, S. Madhi, N. S. Chowdari, M. L. Kantam and B. J. Sreedhar, *J. Am. Chem. Soc.*, 2002, **124**, 14127.
- P. J. Ellis, I. J. S. Fairlamb, S. F. J. Hackett, K. Wilson, A. F. Lee, *Angew. Chem. Int. Ed.*, 2010, **49**, 1820.
- L. Shao, B. Zhang, W. Zhang, S. Y. Hong, R. Schlägl, D. S. Su, *Angew. Chem.* 2013, **125**, 2168; *Angew. Chem. Int. Ed.* 2013, **52**, 2114.
- J. J. Davis, K. S. Coleman, K. L. Busuttill and C. B. Bagshaw, *J. Am. Chem. Soc.*, 2005, **127**, 13082; J. J. Davis, C. B. Bagshaw, K. L. Busuttill, Y. Hanyu, K. S. Coleman, *J. Am. Chem. Soc.*, 2006, **128**, 14135.
- A. K. Kakkar, *Chem. Rev.*, 2002, **102**, 3579.
- Z. Fu, T. Li, B. Mu, L. Mao, G. Li, W. Xu, Y. Wu, *J. Mol. Catal. A: Chem.*, 2012, **200**, 363;
- N. Zhao, T. Li, Z. Zhai, J. Qiu, W. Xu, H. Liu, Y. Wu, *ChemCatChem.*, 2013, **5**, 1481.
- J. S. Sharp, D. J. Farmer and J. Kelly, *Langmuir*, 2011, **27**, 9367.
- K. Sakakibara, H. Kamitakahara, T. Takano, and F. Nakatsubo. *Biomacromolecules*, 2007, **8**, 1657.
- Z. Fu, N. Zhang, J. Liu, T. Li, W. Xu, F. Wang, T. Wang, Z. Zhai, L. Liu, L. Mao, Y. Wu, *J. Colloid Interface Sci.* 2013, **394**, 409.
- C. Copéret, M. Chabanas, R. Petroff Saint-Arroman and J-M. Basset, *Angew. Chem. Int. Ed.*, 2003, **42**, 156; X. Huang, Y. Li, Y. Chen, E. Zhou, Y. Xu, H. Zhou, X. Duan, and Y. Huang* *Angew. Chem. Int. Ed.*, 2013, **52**, 2520.
- S. Schauer mann, N. Nilius, S. Shaikhutdinov and H-J Freund, *Acc. Chem. Res.*, 2013, **46**, 1673; Q. Fu, F. Yang and X. Bao, *Acc. Chem. Res.*, 2013, **46**, 1692.
- K. Köhler, W. Kleist and S. S. Pröckl, *Inorg. Chem.*, 2007, **46**, 1876; F. Y. Zhao, M. Shirai, Y. Ikushima and M. Arai, *J. Mol. Catal. A: Chem.*, 2002, **180**, 211.
- a) S. S. Soomro, F. L. Ansarib, K. Chatziapostolou, K. Köhlera, *J. Catal.* 2010, **273**, 138. b) B. Crociani, S. Antonaroli, A. Marini, U. Matteoli, A. Scrivanti, *Dalton Trans.* 2006, 2698.
- G. R. Cairns, R. J. Cross, D. Stirling, *J. Mol. Catal. A: Chem.* 2001, **172**, 207.
- F.C. Loh, K.L. Tan, E.T. Kang, *Eur. Polym. J.* 1991, **27**, 1055.
- J. Zou, S. G. Stewart, C. L. Raston, K. S. Iyera, *Chem. Commun.* 2011, **47**, 1803.
- The boron related peaks (192.5 eV BE) was the adsorption of excessive ArB(OH)₂; The bromine related peaks (68.1 eV BE) might arise from residual bromide associated with the oxidative addition step after the catalysis.
- About ppm Pd sufficient for cross-coupling reaction: S D Walker, T E Barder, J R Martinelli, S L Buchwald, *Angew Chem Int Ed.* 2004, **43**, 1871; M R Biscoe, B P Fors, S L Buchwald. *J Am Chem Soc.* 2011, **133**, 16707. B P Fors, D A Watson, M R Biscoe, S L Buchwald. *J Am Chem Soc.* 2008, **130**, 13552. T E Barder, S D Walker, J R Martinelli, S L Buchwald. *J. Am. Chem. Soc.*, 2005, **127**, 4685.

Entry for the Table of Contents

Evidences of Pd catalytic cycle

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Jie Liu, and Yangjie Wu*

The Recyclable Cyclopalladated
Ferrocenylimine Self-assembly Film: A
System for Mechanism Investigation of
Heterogeneous Catalysis



The cyclopalladated ferrocenylimine self-assembly film, grafting onto solid substrate surfaces by covalent bond, exhibited efficiently, reusability and stability in Suzuki-Miyaura reaction. A cycle of Pd^{II} to Pd⁰ and Pd⁰ to Pd^{II} on the surface was clearly detected and illustrated. Pd⁰ in the SAM-films as an active surface acted as heterogeneous catalyst to catalyse the coupling reaction.