RSC Advances

PAPER

Cite this: RSC Adv., 2014, 4, 26413

Received 23rd March 2014 Accepted 14th April 2014 DOI: 10.1039/c4ra02540g www.rsc.org/advances

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

The recyclable cyclopalladated ferrocenylimine self-assembly catalytic film and investigation of its role in the mechanism of heterogeneous catalysis[†]

Zhihua Fu, Tiesheng Li,* Xiaohang He, Jie Liu and Yangjie Wu*

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 bonds. Water contact angle, ultraviolet-visible spectroscopy (UV-Vis), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), low-angle X-ray diffraction (LAXD) and cyclic voltammetry (CV) were used to characterize the structural and compositional information of the modified surfaces. The immobilized catalyst films were tested for the 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. 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 times were explored in detail, 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 the coupling reaction of aromatic halides and borophenylic acid proceeded *via* a mechanism of surface-catalyzed process.

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 palladiumcatalyzed reaction in neat water under heterogeneous catalysis7 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, polyvinylpyrrolidone, chitosan, etc.),* hybrid organic-inorganic supports (Pad/SiO2, Pad/PMO, Pad/ SBA-15, silica, zeolite and metal oxide-supported ionic liquids, etc.)9 and inorganic supports (Pad/C, metal oxides, sepiolite, hydroxyapatite, hydrotalcite, mesoporous silica, etc.)10 have 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 the current studies in heterogeneous catalysis.12 It is anticipated that help in improving the catalytic systems will come from a careful examination of the heterogeneous mechanism.

In the primary mechanism of the coupling reactions catalyzed by solid-supported Pd it is accepted that Pd catalysts catalyze in a homogeneous way by leaching Pd species,¹³ which



View Article Online

View Journal | View Issue

The College of Chemistry and Molecular Engineering, Zhengzhou University, 75 Daxue Road, Zhengzhou 450001, P.R. China. E-mail: lts34@zzu.edu.cn; wyj@zzu.edu.cn † Electronic supplementary information (ESI) available. See DOI: 10.1039/c4ra02540g

can re-deposit when the reaction comes to an end. Rapid development of sophisticated experimental techniques and theoretical modelling14 in recent years has allowed an unprecedented insight into the molecular nature of the very complex reactions taking place on the catalyst surface as well as leaching of 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 was considerable circumstantial evidence that in the latter materials, surface sites may play a direct role in the catalytic cycle.17 Both Ellis18 and Shao19 showed evidence 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 being carried out, unequivocal evidence for surface-catalyzed cross-coupling chemistry remain elusive. Clearly, the study of palladium based coupling reactions will continue and potential breakthroughs in the elucidation of the dynamics of palladium and the determination of the type(s) of palladium species which are 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 films²¹ (Langmuir-Blodgett (LB) films, self-assemble films, etc.) on solid slides can be characterized, identified, and the nature of the surface species by a variety of experimental techniques cab be determined. That enables thin films to be an ideal model system to study surface and interface behaviour, with which we can gain a more in-depth insight into the catalytic behaviour and mechanisms at the nanomolecular level.

Our recent studies have found that molecule orientation and morphology of cyclopalladated ferrocenylimine 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 the catalytic reaction.22 However, the LB films desorbed from the solid slides to some extent when it was placed in organic solvents or under heating conditions, which affected the experimental results. Then cyclopalladated arylimine self-assembled 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 the film was unclear, which made it difficult to discuss the catalytic mechanism. So, rational design of suitably catalysts should be closely linked to deeper insights into the mechanisms involved at the 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 ferrocenylimine catalysts onto solid surfaces by covalent bonds and evaluate the activity and recyclability of the resulting composites in the Suzuki–Miyaura reaction. By characterizing, identifying, and estimating the nature of the surface species, we will provide strong evidence that the heterogeneous Suzuki–Miyaura reaction catalyzed by catalytic nano-sheet film proved to be a surface catalytic process.

Results and discussion

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

Preparation of cyclopalladated ferrocenylimines nano-sheet films which grafted onto silicon, glass and quartz surfaces was illustrated in Scheme 1. The wafers were hydrophilically 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 ferrocenylimines for 48 h to obtain **Si-CDI-Pd**.

The amount of Pd in **Si-CDI-Pd** was 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 surface wettability which was caused by either a chemical gradient or a gradient in the topographical surface structure.²⁴ Water contact angles on modified solid surfaces are shown in Fig. 1.

After pre-treatment with "piranha" solution, the silicon and quartz substrate became strongly hydrophilic because it had an extremely low water contact angle (5°), which gave rise to water contact angles of 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 ferrocenylimines. The changes in water contact angles of modified solid surfaces indicated that the surface configuration had significant changed, which could clearly reflect the chemical gradient of each step. It also meant that the catalyst films on solid substrates were obtained by the self-assembly method. UV-vis absorption spectra of modified quartz plates along with the immobilization process offered further evidence of the synthesis of **Si-CDI-Pd** (Fig. S1†).

In order to understand the more detailed information of the catalyst structure, composition, the influence of the supporting substrate with the prospect of obtaining even more efficient



Scheme 1 Preparation of cyclopalladated ferrocenylimine nanosheet films (Si-CDI-Pd).



Fig. 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 ferrocenylimines).

catalysis, AFM images (Fig. 2) and XPS spectra (Fig. 3) were measured at different steps of the surface derivatization process of **Si-CDI-Pd**.

The XPS spectra covered the Br 3d, Si 2p, Cl 2p, C 1s, N 1s, Fe 2p3 and Pd 3d5 energy ranges. The O 1s core level is not shown here because it gave no useful information. The obtained XPS of the clean silicon wafer only gave two Si 2p peaks (99.1 eV BE, 103.0 eV BE) attributed to bulk elemental Si and silicon oxide is also not displayed. The binding energies (BEs) obtained for all core-level spectra presented here are summarized in Table S1.†

The composition and morphology of the silicon wafer immobilization process of **Si-CDI-Pd** are shown below. The AFM images acquired on the clean wafer (Fig. 2a) revealed a flat and evenly aligned surface with 0.41 nm rms. And then a smooth and homogeneous surface with a *ca.* 0.56 nm rms image (Fig. 2b) was observed after silanization. The binding energies of C1s, N1s, and Si2p contributed at about 228.4 eV, 399.1 eV, 99.1 eV and 102.6 eV respectively at this step. Although no new element was detected in the spectrum (Fig. 3) except for a shoulder spectrum 289.1 eV BE of C1s, the AFM images obtained after CDI addition (Fig. 2c) exhibited a higher rms than that observed after silanization (1.5 nm), which indicated



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

that CDI could be introduced. High resolution XPS narrow scan for the Pd3d level showed $3d_{3/2}$ and $3d_{5/2}$ at 343.2 eV and 337.9 eV, Cl2p level at 198.0 eV and Fe2p at 708.4 eV BE, which indicated that the cyclopalladated ferrocenylimine was attached (Fig. 3). AFM investigation of the catalyst-grafted surface (Fig. 2d) presented evidence of high-density arrays and an orderly structure regardless of a few clusters, resulting in a lower rms of the surface rms down to 1.0 nm.

Electrochemical measurements of **Si-CDI-Pd** on ITO electrodes were carried out in a conventional three-electrode configuration using a saturated calomel electrode as the reference electrode and Ag/AgCl as the counter electrode. Fig. 4 shows 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 are shown in Fig. S2.† All the potential values are 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 ($\Delta E_{\rm p} = E_{\rm pa} - E_{\rm pc}$) 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 to the structure of cyclopalladated ferrocenylimines films grafted on glass electrodes. The low

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



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

electroactivity of the catalyst films is 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 variation 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 (Fig. S3†). CV and AFM investigation of the catalystgrafted surface presented the evidence of high-density arrays and an orderly structure. The ordered structure and the stability of catalyst in **Si-CDI-Pd** demonstrated by these measurements may influence the catalysis performance of the nano-sheet film, which prompted us to explore the surface chemical reactions in the heterogeneous catalysis system.

Heterogeneous catalytic properties of Si-CDI-Pd

As mentioned earlier, the Suzuki cross-coupling reaction usually serves as a model for characterization of new catalysts and optimization of reaction conditions. 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 selfassembled film catalysts have been reported but all of them were with a higher catalyst loading.¹¹

The catalytic activity of **Si-CDI-Pd** was evaluated in the 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 (ESI†) clearly showed that it was a heterogeneous catalytic process. **Si-CDI-Pd** displayed a much higher catalytic activity even with less catalyst loading, which yielded 99% 4-methylbiphenyl as the only product compared with their analogous 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

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 yield probably due to the electronic effects (entries 7 and 8). For arylboronic acid, the conversion was excellent (entries 9–12), except for pyrimidine which was obtained in moderate yield (64%, entry 11), indicating that **Si-CDI-Pd** was efficient for the Suzuki–Miyaura reaction in a heterogeneous system. The conditions used above were also competitive in terms of the ligand and solvent.¹⁷ For each substrate, no ligands conferred the higher activity to Pd in neat water.

Nevertheless, there has been little discussion about whether the surface could influence the catalytic properties in the reported Suzuki reaction involving SAMs²¹ or not,¹⁵ which was an important factor for the heterogeneous catalytic system. The absence of a negative effect of the surface might be due to the presence of the orderly arranged 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 bottomed 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 operations²³ as depicted in Scheme 2.

In the case of **Si-CDI-Pd**, although a decreased yield was observed after eight reaction cycles, a moderate yield was still obtained after tenth cycle. There was no catalyst deterioration observed, confirming the high recyclability and stability of the heterogeneous catalysts (Fig. 5b). ICP-AES measurement showed trace amounts of Pd-leaching during the recycling process (Table S4[†]). However, the reaction time had to be prolonged to 18 h after six cycles. A similar observation was

Table 1	The Suzuki-Miyaura	reaction of phenylboronic a	id with 4-bromotoluene	e catalysed by catalys	st or blank quartz plate ^a
---------	--------------------	-----------------------------	------------------------	------------------------	---------------------------------------

$H_3C - \swarrow Br + \swarrow B(OH)_2 \xrightarrow{\text{cat., } K_2CO_3} H_3C - \boxtimes B(OH)_2 \xrightarrow{\text{cat., } K_2CO_3} H_3C - \boxtimes B(OH)_2 \xrightarrow{\text{cat., } K_2CO_3} H_3C - \boxtimes B(OH)_2 \xrightarrow{\text{cat., } K_2CO_3} \xrightarrow{\text{cat.,$

Entry	Catalytic system	Catalyst/10 ⁻⁶ mmol	Time/h	Product	$\operatorname{Yield}^{b}(\%)$	TON
1	Si-CDI-Pd	7.6	12	<i>p</i> -CH ₃ -Ph-Ph	99	16 283
2	Homogeneous	1000	24	p-CH ₃ -Ph-Ph	90	113
3 ^c	Homogeneous	500	24	<i>p</i> -CH ₃ -Ph-Ph	73	182
4	Homogeneous	50	48	p-CH ₃ -Ph-Ph	Trace	_
5	Quartz plate	_	48	<i>p</i> -CH ₃ -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, 12 h. Quartz plate ($30 \times \text{mm} \times 10 \text{ mm} \times 1 \text{ mm}$). ^{*b*} Yields determined by HPLC, based on the products. ^{*c*} PhB(OH)₂ 0.3 mmol.

Table 2 Suzuki reaction of arylboronic acid with aryl halides catalysed by Si-CDI-Pd (round-bottomed flask)^{*a*}



Ar–Br	Ar-B(OH) ₂	Product	$\operatorname{Yield}^{b}(\%)$
<i>p</i> -NO ₂ -Ph	Ph	<i>p</i> -NO ₂ -Ph-Ph	99
<i>p</i> -CH ₃ O-Ph	Ph	<i>p</i> -CH ₃ O-Ph-Ph	97
<i>p</i> -NC-Ph	Ph	<i>p</i> -NC-Ph-Ph	98
<i>p</i> -F ₃ C-Ph	Ph	<i>p</i> -F ₃ C-Ph-Ph	71
<i>p</i> -H ₂ N-Ph	Ph	<i>p</i> -H ₂ N-Ph-Ph	97
1,3-Dimethy-Ph	Ph	1,3-Dimethy-Ph-Ph	80
2-Bromo pyridine	Ph	2-Bromo-Py-Ph	60
1-Bromon-NP	Ph	1-Bromon-NP-Ph	34
<i>p</i> -Me-Ph	<i>p</i> -OCH ₃ -Ph	<i>p</i> -OCH ₃ -Ph-Ph-(<i>p</i> -Me)	85
<i>p</i> -Me-Ph	1,3-Difluoro-Ph	1,3-Difluoro-Ph-Ph-(<i>p</i> -)Me	99
<i>p</i> -Me-Ph	Pyrimidine	Pyrimidine-Ph-(<i>p</i> -)Me	64
<i>p</i> -Me-ph	5-(Methoxycarbonyl)-2-methyl-Ph	5-(Methoxycarbonyl)-2-methyl-Ph-Ph-(p-)Me	96
	Ar-Br p-NO ₂ -Ph p-CH ₃ O-Ph p-NC-Ph p-F ₃ C-Ph p-H ₂ N-Ph 1,3-Dimethy-Ph 2-Bromo pyridine 1-Bromon-NP p-Me-Ph p-Me-Ph p-Me-Ph p-Me-Ph p-Me-Ph p-Me-ph	Ar-BrAr-B(OH)_2 p -NO ₂ -PhPh p -CH ₃ O-PhPh p -CPhPh p -NC-PhPh p -R ₃ C-PhPh p -H ₂ N-PhPh1,3-Dimethy-PhPh2-Bromo pyridinePh1-Bromon-NPPh p -Me-Ph p -OCH ₃ -Ph p -Me-Ph p -OCH ₃ -Ph p -Me-Ph p -OtH ₃ -Ph p -Me-Ph p -OtH ₃ -Ph p -Me-Ph p -minidine p -Me-Ph p -minidine p -Me-Ph p -(Methoxycarbonyl)-2-methyl-Ph	Ar-BrAr-B(OH)_2Product p -NO ₂ -PhPh p -NO ₂ -Ph-Ph p -CH ₃ O-PhPh p -CH ₃ O-Ph-Ph p -NC-PhPh p -CH ₃ O-Ph-Ph p -NC-PhPh p -NC-Ph-Ph p -F ₃ C-PhPh p -F ₃ C-Ph-Ph p -H ₂ N-PhPh p -H ₂ N-Ph-Ph1,3-Dimethy-PhPh1,3-Dimethy-Ph-Ph2-Bromo pyridinePh2-Bromo-Py-Ph1-Bromon-NPPh1-Bromon-NP-Ph p -Me-Ph p -OCH ₃ -Ph p -OCH ₃ -Ph-Ph-(p -Me) p -Me-Ph p -jifluoro-Ph1,3-Difluoro-Ph-Ph-(p -)Me p -Me-PhS-(Methoxycarbonyl)-2-methyl-Ph5-(Methoxycarbonyl)-2-methyl-Ph

^{*a*} Reaction conditions: phenylboric 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*} Isolated yield. ^{*c*} NP: naphthyl.



Scheme 2 Illustration of the reaction operations used in flask reactors.



Fig. 5 Recycling experiments of the Suzuki-Miyaura reaction catalyzed by Si-CDI-Pd. (a) Isolated yield.

presented by other researchers of retained high yield with decreasing activities (or lengthened reaction time) upon recycling 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 the Pd active center in the catalytic process, which could be further proved by CV tests (Fig. S4†).

Plausible heterogeneous mechanism

Researchers have used surface science methods²⁷ and metal single crystals²⁸ to explore elementary processes in heterogeneous catalysis, 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 research on the heterogeneous catalytic process leaves questions about the generality and validity of such mechanistic studies. It is well known that the changes of surface during the catalytic process are the key factor for elucidating the catalytic mechanism. Thus, our aim is focused on insight into what the nature of the activities is by utilizing more realistic procedures which could capture part of the complexity inherent to heterogeneous catalysis.

Plots of conversion *versus* reaction time for the Suzuki reaction was shown in Fig. 6. Quantitative conversions were obtained within 12 h. The corresponding analysis of CV (Fig. S5†), AFM images and water contact angles acquired at different reaction times were precisely investigated (Fig. 7). Significant morphology changes of silicon wafer grafted with catalysts were observed during catalytic processes, with which a detailed analysis of the catalytic processes is presented.



Fig. 6 Isolated yield of Suzuki–Miyaura reaction catalyzed by Si-CDI-Pd at different reaction times.

Fig. 7a showed smooth, ordered 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. Fig. 7b-e shows the surface morphologies of Si-CDI-Pd at different reaction times, in which remarkable morphological changes of the 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 (Fig. 7e) at 6-h catalysis, which revealed that the drastic catalytic process occurred. A uniform, homogeneous and ordered pattern reappeared in Fig. 7f when the catalytic reaction was completed. These results indicated that Si-CDI-Pd as a heterogeneous catalyst catalyzed coupling of aromatic halides and borophenylic acid proceeded via a 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, which could be illustrated by the surface changes made by the catalytically active Pd on the 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 to try to elucidate the processes proposed (Fig. 8a).

Studies of XPS spectra may provide more information about the dynamics of catalytically 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 Pd^{0} and Pd^{0} to Pd^{II} of the cyclopalladated ferrocenylimines on the surface of **Si-CDI-Pd** (Fig. 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



Fig. 7 AFM images of Si-CDI-Pd at different reaction times in the Suzuki–Miyaura reaction. (a) 0 h, (b) 0.5 h, (c) 1 h, (d) 3 h, (e) 6 h, and (f) 12 h. Insets are water contact angles.



Fig. 8 (a) The speculation of **Si-CDI-Pd** at different catalysis times in the 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).

and 338.3 eV BE corresponding to the Pd3d core level. Reduced Pd^{II} to catalytic active Pd^{0} could be seen in the whole process of catalysis reaction and oxidation state of Pd^{0} to Pd^{II} in reaction with PhBr was also confirmed by XPS spectra.

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 the catalytic cycle. The decrease of Pd^{II} (BE 343.3, 338.1 eV) intensity was found to give direct evidence of reduction of Pd^{II} to Pd⁰ in the presence of phenylboronic acid in Suzuki reactions³⁰ The broadening FWHM of the Pd^{II} peak (1.98 eV BE and 1.79 eV BE) suggested that different oxidized forms of palladium are 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 in the XPS spectrum after 1 h catalysis, which was attributed to the coexistence of Pd⁰ species and Pd^{II} species (even of Pd^I (ref. 31)). This 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 oxidation additions (Pd(PhBr)L_x),³² are presented as the occurrence of oxidative additions in the catalytic process.

Main Pd⁰ (BE 340.5, 335.2 eV) and minor Pd^{II} (BE 343.2, 337.6 eV) are shown in Fig. 2d. The major of Pd⁰ demonstrated the evidence 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 $[Bu_4N]_2[PdBr_4]$. This species on the surface might arise from residual bromide from the catalytic process, which is known to be catalytically active at forming Br–Pd–aryl intermediates.³³

The bromine in the Br3d spectrum reduced to 68.3 eV BE which was very close to that found for $[Pd(PhBr)L_x]$ which also showed continuous oxidative additions in the 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 the coupling of aromatic halides and borophenylic acid proceeded via a mechanism of surface-catalyzed reactions as follows: First, Pd^{II} was reduced by activation of ArB(OH)₂ in situ to Pd⁰ on the surface of the catalyst 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 a synergic way to form intermediates. Finally, the 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 molecules.

Conclusions

In this article, an efficient, reusable and stable Pd nano-sheet film was developed by immobilized cyclopalladated ferrocenylimines onto a solid slice. The order, orientation structure catalysts in **Si-CDI-Pd** were demonstrated by AFM measurements. **Si-CDI-Pd** was tested in the Suzuki–Miyaura reaction and displayed a higher catalytic activity even with a lower catalyst loading³⁵ for the preparation of various biaryls at elevated temperature 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 removing and washing, which was satisfies the requirement of green, sustainable and economical chemistry. Good stability and reusability are presented; 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 times was explored in detail. **Si-CDI-Pd** acted as a heterogeneous catalyst to catalyse the Suzuki–Miyaura reaction carried through a surface-catalysis process. The cycle of Pd^{II} to Pd⁰ and Pd⁰ to Pd^{II} on the surface was clearly detected and illustrated. There was also evidence 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 in a 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 catalysts and reaction mechanisms which is very important since this often provides a rational way to improve catalytic activity and selectivity.

Acknowledgements

We are grateful to the National Natural Science Foundation of China (no. 20973157), Research and Development Foundation of Zhengzhou (094SGZG23056); Prof. Minghua Liu, Penglei Chen for XPS measurements; Prof. Luyuan Mao for AFM analysis.

Notes and references

- 1 Cross-Coupling Reactions. A Practical Guide, *Topics in Current Chemistry*, ed. N. Miyaura, Springer Verlag, Berlin, 2002; *Metal Catalyzed Cross-Coupling Reactions*, ed. A. de Meijere and F. Diederich, Wiley-VCH, Weinheim, 2nd edn, 2004; S. L. Buchwald, *Acc. Chem. Res.*, 2008, **41**, 1439.
- 2 C. Torborga and M. Beller, Adv. Synth. Catal., 2009, 351, 3027;
 G. Zeni and 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, 346, 1553; X. F. Wu, P. Anbarasan, H. Neumann and M. Beller, Angew. Chem., Int. Ed., 2010, 49, 9047.
- 3 J.-C. Hierso, M. Beaupérin and P. Meunier, *Eur. J. Inorg. Chem.*, 2007, 3767.
- 4 M. Butters, D. Catterick, A. Craig, A. Curzons, D. Dale, A. Gillmore, S. P. Green, I. Marziano, J.-P. Sherlock and W. White, *Chem. Rev.*, 2006, **106**, 3002; J. Magano and J. R. Dunetz, *Chem. Rev.*, 2011, **111**, 2177–2250.
- 5 J. A. Gladysz, *Pure Appl. Chem.*, 2001, **73**, 1319; A. Fukuoka and P. L. Dhepe, *Chem. Rec.*, 2009, **9**, 224.
- 6 Á. Molnár, *Chem. Rev.*, 2011, **111**, 2251;
 A. Dhakshinamoorthy, M. Opanasenko, J. Čejka and H. Garcia, *Adv. Synth. Catal.*, 2013, **355**, 247.
- 7 M. Lamblin, L. Nassar-Hardy, J.-C. Hierso, E. Fouquet and F.-X. Felpin, Adv. Synth. Catal., 2010, 352, 33; B. Yuan, Y. Pan, Y. Li, B. Yin and H. Jiang, Angew. Chem., Int. Ed., 2010, 49, 4054; S. Ogasawara and S. Kato, J. Am. Chem. Soc., 2010, 132, 4608; J. Wei, J. Jiao, J. Feng, J. Lv, X. Zhang, X. Shi and Z. Chen, J. Org. Chem., 2009, 74, 6283; R. Franzén and Y. J. Xu, Can. J. Chem., 2005, 83, 266.
- 8 For polyaniline: P. Boomi, H. G. Prabu and J. Mathiyarasu, *Eur. J. Med. Chem.*, 2014, 72, 18. For polymeric imidazole:
 Y. M. Yamada, S. M. Sarkar and Y. Uozumi, *J. Am. Chem. Soc.*, 2012, 134, 3190, For poly(vinylpyrrolidone): Y. Li, E. Boone and M. A. El-Sayed, *Langmuir*, 2002, 18, 4921. For chitosan: J. J. E. Hardy, S. Hubert, D. J. Macquarrie and A. J. Wilson, *Green Chem.*, 2004, 6, 53.
- 9 For Pd/SiO2: M. Kim, J. C. Park, A. Kim, K. H. Park and H. Song, *Langmuir*, 2012, 28, 6441, For Pd/PMO: B. Karimi, D. Elhamifar, J. H. Clark and A. J. Hunt, *Org. Biomol. Chem.*, 2011, 9, 7420. For Pd/SBA-15: J. Zhi, D. Song, Z. Li, X. Lei and A. Hu, *Chem. Commun.*, 2011, 47, 10707. For silica: Z. Chen, Z.-M. Cui, F. Niu, L. Jiang and W.-G. Song, *Chem. Commun.*, 2010, 46, 6524.

- 10 For Pd/C: H. Sakurai, T. Tsukuda and T. Hirao, J. Org. Chem., 2002, 67, 2721. For metal oxides: P. D. Stevens, G. Li, J. Fan, M. Yen and Y. Gao, Chem. Commun., 2005, 4435. For sepiolite: K. Shimizu, R. Maruyama, S. Komai, T. Kodama and Y. Kitayama, J. Catal., 2004, 227, 202. For hydroxyapatite: R. M. Mohamed and E. S. Baeissa, Appl. Catal., A, 2013, 464–465, 218. For hydrotalcite: M. Mora, C. Jiménez-Sanchidrián and J. R. Ruiz, J. Mol. Catal. A: Chem., 2008, 285, 79. For mesoporous silica: W. Fang, J. Yang and J. Gong, Adv. Funct. Mater., 2012, 22, 842.
- 11 L. Jin and J. Liebscher, Chem. Rev., 2007, 107, 133.
- 12 N. T. S. Phan, M. V. D. Sluys and C. W. Jones, *Adv. Synth. Catal.*, 2006, **348**, 609.
- 13 J.-S. Chen, A. N. Vasiliev, A. P. Panarello and J. G. Khinast, *Appl. Catal.*, A, 2007, 325, 76; Z. Niu, Q. Peng, Z. Zhuang, W. He and Y. Li, *Chem.-Eur. J.*, 2012, 18, 9813.
- 14 L. Xue and Z. Lin, Chem. Soc. Rev., 2010, 39, 1692.
- 15 M. Pérez-Lorenzo, J. Phys. Chem. Lett., 2012, 3, 167.
- 16 S. MacQuarrie, J. H. Horton, J. Barnes, K. McEleney, H.-P. Loock and 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.
- 18 P. J. Ellis, I. J. S. Fairlamb, S. F. J. Hackett, K. Wilson and A. F. Lee, Angew. Chem., Int. Ed., 2010, 49, 1820.
- 19 L. Shao, B. Zhang, W. Zhang, S. Y. Hong, R. Schlçgl and D. S. Su, Angew. Chem., 2013, 125, 2168; Angew. Chem., Int. Ed., 2013, 52, 2114.
- 20 J. J. Davis, K. S. Coleman, K. L. Busuttil and C. B. Bagshaw, *J. Am. Chem. Soc.*, 2005, **127**, 13082; J. J. Davis, C. B. Bagshaw, K. L. Busuttil, Y. Hanyu and K. S. Coleman, *J. Am. Chem. Soc.*, 2006, **128**, 14135.
- 21 A. K. Kakkar, Chem. Rev., 2002, 102, 3579.
- 22 Z. Fu, T. Li, B. Mu, L. Mao, G. Li, W. Xu and Y. Wu, *J. Mol. Catal. A: Chem.*, 2012, **200**, 363.
- 23 N. Zhao, T. Li, Z. Zhai, J. Qiu, W. Xu, H. Liu and Y. Wu, *ChemCatChem*, 2013, 5, 1481.
- 24 J. S. Sharp, D. J. Farmer and J. Kelly, *Langmuir*, 2011, 27, 9367.

- 25 K. Sakakibara, H. Kamitakahara, T. Takano and F. Nakatsubo, *Biomacromolecules*, 2007, **8**, 1657.
- 26 Z. Fu, N. Zhang, J. Liu, T. Li, W. Xu, F. Wang, T. Wang, Z. Zhai, L. Liu, L. Mao and Y. Wu, *J. Colloid Interface Sci.*, 2013, **394**, 409.
- 27 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.
- 28 S. Schauermann, 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.
- 29 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.
- 30 (a) S. S. Soomro, F. L. Ansarib, K. Chatziapostoloua and K. Köhlera, J. Catal., 2010, 273, 138; (b) B. Crociani, S. Antonaroli, A. Marini, U. Matteoli and A. Scrivanti, Dalton Trans., 2006, 2698.
- 31 G. R. Cairns, R. J. Cross and D. Stirling, J. Mol. Catal. A: Chem., 2001, 172, 207.
- 32 F. C. Loh, K. L. Tan and E. T. Kang, *Eur. Polym. J.*, 1991, 27, 1055.
- 33 J. Zou, S. G. Stewart, C. L. Raston and K. S. Iyera, *Chem. Commun.*, 2011, 47, 1803.
- 34 The boron related peaks (192.5 eV BE) were due to 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.
- 35 About ppm Pd sufficient for cross-coupling reaction:
 S. D. Walker, T. E. Barder, J. R. Martinelli and
 S. L. Buchwald, Angew. Chem., Int. Ed., 2004, 43, 1871;
 M. R. Biscoe, B. P. Fors and S. L. Buchwald, J. Am. Chem. Soc., 2011, 133, 16707;
 B. P. Fors, D. A. Watson,
 M. R. Biscoe and S. L. Buchwald, J. Am. Chem. Soc., 2008, 130, 13552;
 T. E. Barder, S. D. Walker, J. R. Martinelli and
 S. L. Buchwald, J. Am. Chem. Soc., 2005, 127, 4685.