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Palladium Nanoparticle-Embedded Polymer Thin Film “Dip Catalyst” for Suzuki–Miyaura Reaction

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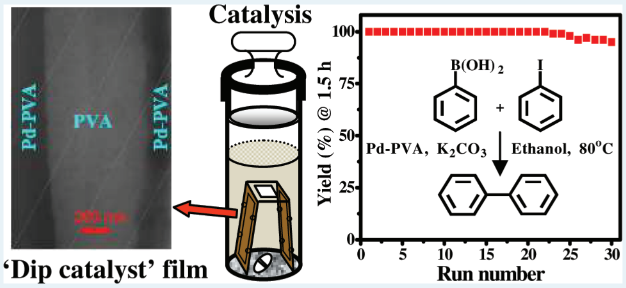
Ⓢ *Supporting Information*

ABSTRACT: Hallmarks of a successful catalyst include simplicity of design and low cost of fabrication, high efficiency, facile recovery and extensive reusability, amenability to monitoring between reuses, and ease of scale up. Even though the number of palladium nanoparticle based catalysts reported for the Suzuki–Miyaura reaction has grown exponentially in recent years, the aforesaid criteria are rarely met in a single system. We present a palladium nanoparticle-embedded polymer thin film which functions as a highly efficient and reusable “dip catalyst” for the Suzuki–Miyaura reaction. The multilayer free-standing nanocomposite thin film is fabricated using a simple in situ process through thermal annealing of a spin-coated film of poly(vinyl alcohol) (PVA) containing the palladium precursor. Fabrication parameters of the Pd-PVA film are optimized for enhanced catalyst efficiency. The catalyst is shown to produce very high yield, turn over number and turn over frequency in the prototypical reaction of iodobenzene with phenylboronic acid. The “dip catalyst” film is easily retrieved from the reaction system and reintroduced in successive batches; the high efficiency is retained beyond 30 cycles. The thin film structure enabled convenient catalyst monitoring by spectroscopy and microscopy between reruns. Efficient use of the catalyst up to 5 mmol scale reaction is demonstrated. A simple figure-of-merit is formulated to quantify the catalyst performance, and the present catalyst is evaluated in the context of those reported earlier. Preliminary exploration of the utility of the thin film catalyst in the Suzuki–Miyaura reaction with several substrates as well as in the Heck and Sonogashira coupling reactions is carried out.



KEYWORDS: *palladium nanoparticle, polymer–metal nanocomposite, thin film, dip catalyst, Suzuki–Miyaura reaction*

■ INTRODUCTION

Efficiency of a catalyst is generally enhanced under homogeneous conditions as it is molecularly dispersed. However the same factor hampers its recovery and reuse. Heterogeneous formulation facilitates recycling, however at the cost of efficiency as the reaction is confined to the interface region. Metal nanoparticles tend toward molecular level efficiency, and deployment in a suitable framework can improve the reusability, paving the way to harnessing the advantages of homogeneous and heterogeneous catalysis. This general concept has motivated extensive explorations. As an example of enormous contemporary interest, we take the case of palladium catalyzed cross coupling reactions, focusing on nanoparticle catalysts and the issue of catalyst recycling. Even though catalyst recovery through nanofiltration[1] and magnetic separation[2] have been used, the procedures are often laborious or the catalyst fabrication elaborate, making the process expensive. Some of the supports that have been used to load the palladium nanoparticle catalyst are mesoporous organosilica and grafted silica foam,[3,4] layered double hydroxide and clays,[5,6] zeolites and molecular sieves,[7−9] various metal oxides,[9,10] activated or nitrogen doped carbon,[9,11,12] and polymeric networks, capsules, and resins.[9,13−15] However, most of these approaches are prone to catalyst leaching or degradation through the repeat cycles, impairing the reaction yields and limiting the reuse. An optimal solution that combines a simple and cheap fabrication of a highly efficient catalyst with effective recovery and reuse, remains elusive.

The concept of a “dip catalyst” that we have developed recently[16] is relevant in this context. The high efficiency and extensive reusability of a catalyst based on silver nanoparticle-embedded poly(vinyl alcohol) (Ag-PVA) thin film fabricated through a simple in situ protocol,[17] in the reduction of 4-nitrophenol by sodium borohydride was demonstrated in that study. Easy fabrication, convenient recycling, and facile monitoring of the “dip catalyst” thin film between uses, are the highlights of this approach. Its generality and versatility stem from the wide variations possible in the catalyst-polymer combinations. Moving beyond the earlier “proof-of-principle” exploration, we now demonstrate the utility of the approach in a reaction of wide applicability in organic synthesis, the palladium catalyzed Suzuki–Miyaura coupling. Choice of this reaction also allows an appraisal of our concept against the

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background of a large collection of nanoparticle catalysts reported earlier.

A survey of the extensive literature on palladium catalyzed Suzuki–Miyaura reaction in particular and the subject of catalysis in general, reveals the critical need to evaluate a catalyst on the basis of multiple parameters. It is desirable to have an integrated view of the various relevant factors including the turn over number (TON) or turn over frequency (TOF), the number of reuse cycles, scale of the reaction, the temperature at which it is carried out (hence the energy input), the solvent/special atmosphere required, and the cost of catalyst fabrication. While quantification of some of these are straightforward, others are complicated. An attempt to evolve a figure-of-merit (FOM) that takes into account as many of the clearly quantifiable factors as possible appears to be worthwhile. Even though FOMs have been invoked for the specific purpose of designing some catalysts,[18] rarely have they been employed for the direct comparison of catalysts available for a chosen reaction. In the present study, we have made a preliminary effort toward this goal which allowed us to make a meaningful comparison of our "dip catalyst" with those reported earlier for the same reaction.

Extending our in situ method for the synthesis of dendritic palladium nanostructures in a PVA film,[19] we have fabricated a multilayer Pd-PVA thin film catalyst. The multilayer structure makes the free-standing film robust while facilitating easy access of the reagents to the ligand-free catalyst nanoparticles embedded and stabilized within the polymer matrix. Experiments are carried out to optimize the Pd/PVA ratio and the reaction conditions for the Suzuki–Miyaura coupling of iodobenzene and phenylboronic acid to yield biphenyl. Under optimal conditions, nearly 100% yield is obtained, and the yield and reaction time shows negligible change over 30 reuses. Very large TONs and TOFs can be realized by using tiny pieces of the catalyst film, and the reaction is found to be facile at scales up to 5 mmol. An FOM of the catalyst is defined incorporating the values of average TOF, number of reuses, scale of the reaction, and the temperature condition required. Using this FOM, we compare the Pd nanoparticle based catalysts reported for this reaction including our "dip catalyst". Finally, the utility of our catalyst in the Suzuki–Miyaura reaction with a range of substrates, as well as in the Heck and Sonogashira reactions is demonstrated.

■ EXPERIMENTAL SECTION

Fabrication of the Catalyst Film. The catalyst film was fabricated by extending the protocol developed in our laboratory earlier.[19] Glass substrates were cleaned by washing and ultrasonication in isopropyl alcohol for 10 min; subsequently they were dried in a hot air oven. A few drops of a solution of polystyrene (PS) (Aldrich, average molecular weight = 280 kDa) in toluene (1 g in 8 mL) was spin-coated using a Laurell Technologies Model WS-400B-6NPP/LITE/8K Photoresist Spinner operated at 1000 rpm for 10 s, and dried at 90 °C for 15 min. Aqueous solutions of K_2PdCl_4 (Aldrich, purity = 99.99% on metal basis) and PVA (Aldrich, average molecular weight = 85–146 kDa, hydrolysis = 99+ %) were mixed in the required proportions; for example, 80 mg of K_2PdCl_4 dissolved in 2 mL of water was mixed with 200 mg of PVA dissolved in 4 mL of water to prepare a film with a Pd/PVA weight ratio, $x = 0.13$. Millipore Milli-Q water (resistivity = 18.2 MΩ cm) was used in all operations. The K_2PdCl_4–PVA solution was coated on top of the PS layer by spinning at 500 rpm for 10 s followed by 6000 rpm for 10 s. After heating the film at 90 °C for 30 min, an aqueous solution of PVA was spin-coated at 500 rpm for 10 s followed by 3000 rpm for 10 s and heated at 90 °C for 30 min; a second coating of PVA was added to increase the thickness. The final layer was formed by spin-coating the K_2PdCl_4–PVA solution as before, and the film was heated at 130 °C for 4 h. It was found that longer heating did not enhance the extent of reduction of the Pd(II) ions or the stability of the film. The film was peeled off the glass substrate and wrapped around a Teflon frame. It was then dipped in toluene to dissolve the PS layer and yield the free-standing 3-layer Pd-PVA/PVA/Pd-PVA film fixed on the frame. The film was finally washed in water to remove the unreduced K_2PdCl_4 and the byproduct KCl formed during the in situ reduction of K_2PdCl_4 by PVA; the observation of KCl and its removal have been discussed in ref 19.

Characterization of the Catalyst Film. The thickness of the film coated on the glass substrate was measured using an Ambios Technology XP-1 Profilometer. Measurement carried out after each spin-coating/heating step provided the thickness of the film at that stage. Cross section samples were prepared by fixing the free-standing film in Araldite resin and cutting into 50 nm thin sections with a Leica ultramicrotome. Field emission scanning electron microscope (FESEM) imaging with energy dispersive X-ray spectroscopy (EDXS) was carried out on a Carl Zeiss model Ultra 55 microscope. Transmission electron microscopy (TEM) was carried out using a Tecnai G2 FEI F12 TEM at an accelerating voltage of 200 kV. Electronic absorption spectra were recorded on a Varian Model Cary 100 UV–visible spectrometer. Chemical composition of the film was analyzed using a Varian 720-ES Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES). Sample for the analysis was prepared by dissolving a known weight of the free-standing film in 100 mL of 60% nitric acid.

Catalysis Studies. All reactions were carried out under normal atmosphere; inert conditions were not required. The procedure followed in a typical reaction is as follows. Two mmol of the base was introduced into a reaction tube in which a magnetic stirring bar was placed. This was followed by the addition of 15 mL of the solvent and 1 mmol of the aryl halide. The catalyst film (thickness ~1 μm, total surface area = 35 cm^2, total weight = 5.62 mg, Pd content = 0.6 μmol)[20] wrapped on a Teflon frame was introduced. After adding 1.1 mmol of phenylboronic acid, the reaction tube was closed with a stopper and keck clip, and introduced into an oil bath preheated to the required temperature. The reaction mixture was stirred with the magnetic bar. Formation of the product was monitored through Gas Chromatograph-Mass Spectrometer (Shimadzu model QP2010) analysis of 0.2 mL samples of the reaction mixture retrieved periodically from the reaction tube. The maximum error in the determination of the reaction time is ~15%; the error is lower for longer reaction times. When the reaction was completed, the catalyst film was taken out and the reaction mixture was filtered; after adding a small amount of silica (Merck, 100–200 mesh), the filtrate was evaporated completely. The residual product was purified through column chromatography and analyzed by NMR (Bruker 500 MHz). The catalyst film taken out of the reaction mixture was dipped briefly in diethyl ether and washed with dichloromethane to remove organic residues, dipped in water and isopropanol to remove the base, and finally dried in vacuum for 30 min. The film was ready for reuse.

RESULTS AND DISCUSSION

The thickness of the different layers of the Pd-PVA/PVA/Pd-PVA catalyst film was determined by profilometer measurements on several samples. Values obtained for the film with $x = 0.13$ (in the Pd-PVA layers) are 0.18 (0.03), 0.53 (0.05), and 0.17 (0.06) μm for the Pd-PVA, PVA, and Pd-PVA layers, respectively.[20] Electronic absorption spectra of the film, recorded through the different stages of fabrication are shown in Figure 1a. The first layer (K_2PdCl_4−PVA) shows the peaks due to the precursor salt; after the short heating step there is little change in the spectrum. The visible change upon coating the second layer (PVA) is due to increased light scattering and the localized surface plasmon resonance (LSPR) absorption of the Pd nanostructures formed in the film; the latter may result from the higher net ratio of PVA to Pd that enhances the chemical reduction of the Pd^{2+} ions.[19] The LSPR peak becomes prominent on heating the 2-layer film for 30 min. As expected, the precursor peaks appear clearly again on coating the third layer (K_2PdCl_4−PVA). The subsequent heating leads to the emergence of the strong LSPR absorption of palladium nanoparticles extending into the visible region; changes become negligible after 4 h of heating. The spectrum of the final film dipped briefly in water[20] indicates the removal of the soluble precursor left unreacted in the film. TEM images of the catalyst film are shown in Figure 1b−d. The first layer shows dendritic structures due to the precursor and some Pd formed on heating;[20] this is consistent with the observation in the precursor-to-palladium nanocrystal transformation investigated in detail earlier.[19] Upon coating the second layer (PVA), the film is too thick to get a clear TEM image; however, one can visualize some morphological changes; spherical particles ∼100−300 nm in diameter are observed. The increased net PVA/Pd ratio and the extended heating contribute to the morphology change.[19] The TEM image of the cross section of the final 3-layer film reveals the layer structure; thickness of the layers are consistent with those noted above. Because of the high density of particles in the outer two layers, individual ones are not resolved, but the low density in the middle layer reveals spherical particles ∼15−30 nm in size. The FESEM image of the cross-section sample combined with EDXS analysis across the layer thickness shows a lower concentration of Pd in the middle layer of the film.[20] The microscopy images are thus consistent with the Pd-PVA/PVA/Pd-PVA coating sequence.

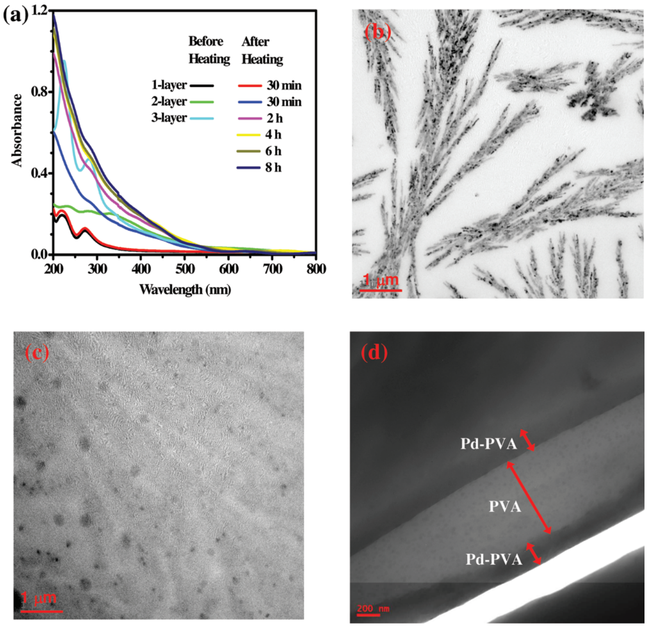

Figure 1. (**a**) Electronic absorption spectra of the catalyst film recorded through the different stages of spin coating and heating. TEM images of the heated (**b**) 1-layer film, (**c**) 2-layer film, and (**d**) final 3-layer film cross section.

A wide range of solvents and bases have been employed in the Suzuki−Miyaura reaction. The catalyst film is robust enough to be used in any of these solvents. However, as the swelling of the polymer film in the solvent enhances the catalyst activity by improving access of the reactants to the catalyst, we have focused in particular on aqueous and alcoholic solvents. We have chosen a film with $x = 0.13$ and a reaction temperature of 80 °C (basis of these choices are discussed below) to investigate the effect of different solvents and bases. All the reactions were carried out using 1 mmol of iodobenzene and 1.1 mmol of phenylboronic acid. Observations with the different solvents (using K_2CO_3 as the base) are collected in Table 1. The rates and yields are poor with pure water and water−ethanol mixtures, but enhanced considerably by the addition of tetrabutylammonium bromide. However, as the base dissolves in the solvent, the product has to be isolated by extraction. Ethanol is an optimal choice of solvent, as there is no need of a phase-transfer agent, the reaction is fast, work up of the reaction mixture is simple, and the yields are quantitative. We have also explored the utility of different bases; Table 2 lists the yields obtained for the reaction run in ethanol for 1.5 h.

Table 1. Time and Yield of the Reaction of Phenylboronic Acid with Iodobenzene in Different Solvents Using K_2CO_3 as the Base and the Thin Film Catalyst (Pd-PVA Layer, $x = 0.13$)[a]

solvent	time (h)	yield (%)
water	5	8
	2[b]	100[b]
water−ethanol (10:1)	5	22
	2[b]	100[b]
water−ethanol (1:1)	5	58
	1.5[b]	100[b]
toluene	3	45
N,*N*-dimethylacetamide	2	100
ethanol	1.5	100

[a] Reaction conditions: 1 mmol of iodobenzene, 1.1 mmol of phenylboronic acid, 2 mmol of K_2CO_3, temperature = 80 °C. [b] With 0.01 mmol of tetrabutylammonium bromide.

Table 2. Yield of the Reaction of Phenylboronic Acid with Iodobenzene in Ethanol Using Different Bases and the Thin Film Catalyst (Pd-PVA Layer, $x = 0.13$)[a]

base	yield (%)	remarks
triethylamine	60	convenient to use
sodium acetate	85	convenient to use
potassium phosphate	100	hygroscopic
sodium hydroxide	100	hygroscopic
potassium carbonate	100	convenient to use

[a] Reaction conditions: 1 mmol of iodobenzene, 1.1 mmol of phenylboronic acid, 2 mmol of base, temperature = 80 °C, time = 1.5 h.

Even though K_2CO_3, K_3PO_4, and NaOH provided similar quantitative yields, K_2CO_3 is preferred as it is nonhygroscopic and easy to handle.

Using ethanol as the solvent and K_2CO_3 as the base, we have carried out several batches of exploratory reactions to determine the optimal value of *x* of the catalyst film and the reaction temperature. It may be noted that only a single product is observed in all the reactions and test runs excluding iodobenzene or phenylboronic acid showed negligible homocoupling reaction. Figure 2 shows the yield as a function of time, when catalyst films with different *x* values are employed; considerable improvement is observed when *x* is increased from 0.07 to 0.13, but there is little enhancement beyond. It is seen that with *x* = 0.13, 100% conversion is achieved in 1.5 h. The TONs for the different catalyst films are not influenced by the reaction temperature. However, the TOFs increase substantially at 80 °C for the films with *x* = 0.13 and 0.15 (Figure 3). The slightly higher TOF obtained using the film with *x* = 0.13 can be attributed to the lower catalyst content and the only marginal increase in the time for 100% conversion.

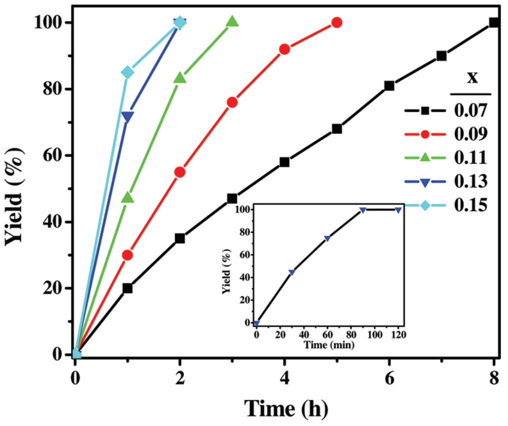

Figure 2. Progress of the Suzuki–Miyaura reaction of phenylboronic acid with iodobenzene in ethanol using K_2CO_3 as the base and the thin film catalyst with different Pd/PVA weight ratios (*x*) in the Pd-PVA layer; reaction conditions: 1 mmol of iodobenzene, 1.1 mmol of phenylboronic acid, 2 mmol of K_2CO_3, temperature = 80 °C. **Inset:** Progress of the reaction using the catalyst with *x* = 0.13 monitored at shorter time intervals.

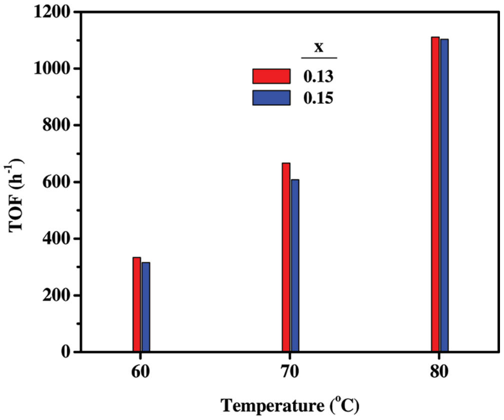

Figure 3. Turn over frequency (TOF) of the Suzuki–Miyaura reaction of phenylboronic acid with iodobenzene in ethanol at different temperatures, using K_2CO_3 as the base and the thin film catalysts with different Pd/PVA weight ratios (*x*) in the Pd-PVA layer; reaction conditions: 1 mmol of iodobenzene, 1.1 mmol of phenylboronic acid, 2 mmol of K_2CO_3.

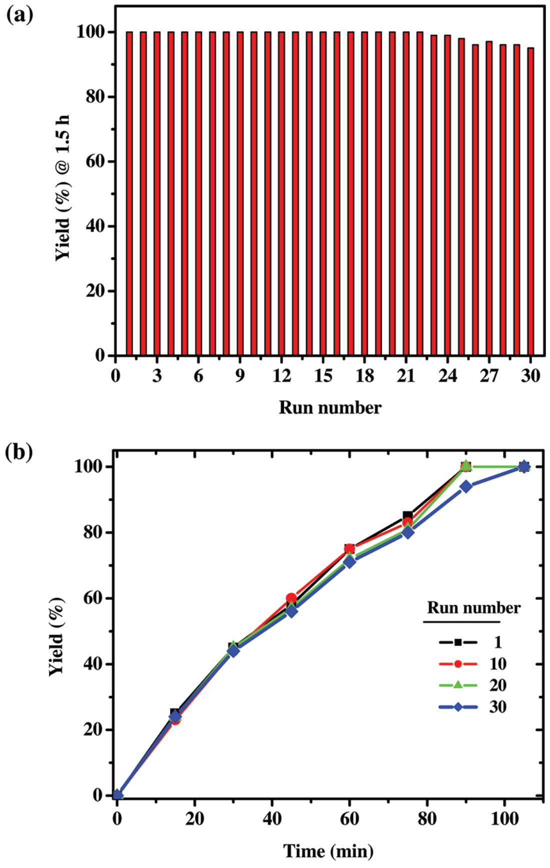

Figure 4. (a) Yield obtained at 1.5 h reaction time in repeated runs of the Suzuki–Miyaura reaction of phenylboronic acid with iodobenzene in ethanol using K_2CO_3 as the base and the same piece of thin film catalyst (Pd-PVA layer, *x* = 0.13); reaction conditions: 1 mmol of iodobenzene, 1.1 mmol of phenylboronic acid, 2 mmol of K_2CO_3, temperature = 80 °C. (b) Kinetics plot showing the yield as a function of time for selected reaction runs.

On the basis of the experiments above, we have chosen the catalyst with *x* = 0.13 (in the Pd-PVA layers), ethanol as the solvent, K_2CO_3 as the base, and a reaction temperature of 80 °C to demonstrate the recycling capability of our "dip catalyst". These reactions were run using 1 mmol of iodobenzene and 1.1 mmol of phenylboronic acid. Nearly 100% yield was obtained in the first run in 1.5 h. The catalyst film was taken out, washed, dried (Experimental Section) and reinserted for the next run. It is found that the same film can be reused extensively. The yields obtained at 1.5 h in the 30 cycles we have run are shown in Figure 4a; it may be noted that 100% yield can be obtained even in the last few cycles by slight increase in the reaction time. Yield of the isolated product from the combined reaction mixtures of the 30 cycles is 89%. The ease of redeployment of the catalyst and the quantitative conversion observed over such a large number of cycles testifies to the versatility of the "dip catalyst" concept. The activity at the end of these runs suggests that the recycling can indeed be continued further. ICP-OES analysis of the catalyst film with *x* = 0.13 used in these reactions indicates that the Pd content is 0.6 μmol.[20] This implies a TON of 1667 in the runs with 100% yield; the total TON for the 30 cycles is the high value of 4.96×10^4. The average TOF works out to be 1102 h^{-1}. We have monitored the progress of the reaction at various points during the repeat cycles. As seen in Figure 4b, the kinetics remains nearly unchanged through the large number of repeated uses.

TEM and X-ray photoelectron spectroscopy (XPS) studies we have carried out earlier[19] have unambiguously proved that the Pd-PVA formed through extended thermal annealing does still contain some amount of unreacted Pd^{2+}. Even though our catalyst film is washed in water following the 4 h heating process, it is possible that it contains trace Pd^{2+}. This may indeed be advantageous for the Suzuki–Miyaura reaction as Pd^{2+} has been implicated in the catalytic cycle.[21] To rule out the possibility of Pd^{2+} alone being the active catalyst, we have attempted the reaction with unheated films of K_2PdCl_4–PVA (with $x = 0.13$). Under identical reaction conditions as above, we find that the reaction hardly proceeds; less than 10% yield is obtained even after 2 h.[20] An experiment in which the Pd-PVA/PVA/Pd-PVA film was removed after 30 min of reaction showed the yield of ~40% reached in that time remaining unchanged for several hours afterward, clearly ruling out the possibility of Pd leached from the film catalyzing the reaction.[20] The extremely low concentration (5 ppb) of Pd detected by ICP-OES analysis in the reaction mixture is clearly insufficient to catalyze the reaction. ICP-OES analysis of a control sample containing all the reagents including the base but no catalyst film showed the Pd content to be <1.0 ppb; this is significant in view of the report[22] of Pd impurity in the base catalyzing the Suzuki–Miyaura reaction. An important advantage of the "dip catalyst" is the ease with which the catalyst can be monitored during the reuse cycles; this is difficult with most of the catalyst immobilization schemes reported earlier. Such examinations provide useful insight into the basis of the durability of the catalyst. The electronic absorption spectra and FESEM images of the catalyst film before the first use and after 15 and 30 cycles of usage are shown in Figure 5. The spectrum shows faint signs of Pd^{2+} generation, but negligible impact on the nanoparticle content, ruling out once again any significant leaching. The microscopy images show that the film morphology is affected very little; but small particles emerge near the surface after extensive recycling. In view of their sizes (compare with Figure 1d) and the EDXS analysis which again indicates that the Pd content is nearly unchanged,[20] we believe that these are Pd nanoparticles. Retention of the morphology of the nanoparticles is a significant observation, as it is different from the case of spherical particles aggregating into needles in solution based catalysts.[23]

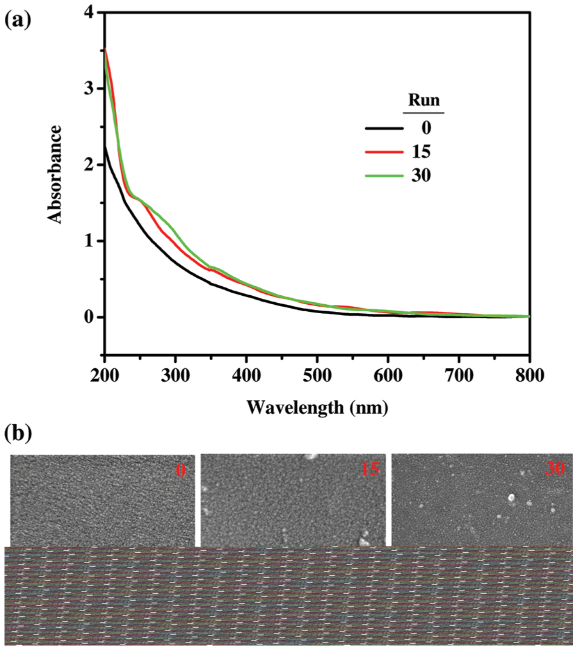

Figure 5. (a) Electronic absorption spectra and (b) FESEM images (scale bar = 100 nm) of the same thin film catalyst (Pd-PVA layer, $x = 0.13$) after different number of uses (zero corresponds to the fresh film) in the Suzuki–Miyaura reaction of phenylboronic acid with iodobenzene in ethanol using K_2CO_3 as the base; reaction conditions for each run: 1 mmol of iodobenzene, 1.1 mmol of phenylboronic acid, 2 mmol of K_2CO_3, temperature = 80 °C.

Very large TONs of the order of 10^5–10^7 have been reported for the Suzuki–Miyaura reaction in recent times.[13,24–31] However, specialized catalyst preparation including high temperature treatments or special reaction conditions,[24–27] catalyst degradation or decline of yield with reuse[13,28] or relatively low reaction yields[29–31] are involved in most cases. To test the high TONs that we can realize, the reaction was carried out with a very small piece of the catalyst film containing 0.014 μmol (14 ppm) of the catalyst; 5 mmol of iodobenzene and 6 mmol of phenylboronic acid were used. Because of the very small size, the film could not be fixed on a Teflon scaffold and hence could not be used in several cycles. However, in just 2 runs, a total TON of 7.2×10^5 could be realized, and a high TOF of 1.1×10^4 h^{-1}. In addition to the efficient circulation in the reaction tube, the smaller size of the film is likely to enhance the accessibility of the Pd nanoparticles embedded within the film contributing to the enhanced TON and TOF. An important factor for the development of a catalyst system is the scale of the reaction that it can be employed in. Figure 6 shows the reaction times for obtaining quantitative conversion in the reactions of 1–5 mmol of iodobenzene, using catalyst films with different areas and hence palladium content. It is seen that with the catalyst film with an area of 35 cm^2, even a 5 mmol scale reaction is satisfactorily completed in a short time; yield of the isolated product is 91%.

Figure 6. Time for completion (100% yield) of the Suzuki–Miyaura reaction of phenylboronic acid with different amounts of iodobenzene in ethanol using K_2CO_3 as the base and different quantities (areas) of the thin film catalyst (Pd-PVA layer, $x = 0.13$); reaction conditions: 1.1 equiv of phenylboronic acid, 2 equiv of K_2CO_3, temperature = 80 °C.

As mentioned earlier, a fair appraisal of the performance of a catalyst for a specific reaction should take into account several parameters. Using the clearly quantifiable ones among them we define the following FOM,

$$\text{FOM} = \frac{(\text{TOF})_{\text{av}} \times N \times S}{298 + |\Delta T|}$$

where $(\text{TOF})_{\text{av}}$ is the average TOF, N the number of runs (cycles), S the maximum scale of reaction demonstrated, and ΔT the magnitude of the deviation in the reaction temperature from the ambient (taken as 298 K). We have carried out a search of the reports on the Suzuki–Miyaura reaction from the year 2000, employing Pd nanoparticles for the specific reaction of iodobenzene with phenylboronic acid. Taking into account all the reports which have provided unambiguous information on the parameters listed above, the FOM of the various catalysts have been estimated. The complete list is provided in the Supporting Information. Those catalysts which exhibit FOMs ≥ 2.0 are represented schematically in Figure 7. As a result of the simultaneous realization of the several beneficial features, our “dip catalyst” scores highest in the list. It is indeed quite possible that the relevant parameters of the various catalysts are not optimized in the reported studies and their FOMs could be enhanced; it is also likely that higher FOMs can be realized for reactions with other substrates or Pd catalysts that are not based on nanoparticles.

Figure 7. Schematic representation of the figure-of-merit (FOM) of various reported catalysts (refs 15, 32–57) and the present thin film catalyst (Pd-PVA layer, x = 0.13) used for the Suzuki–Miyaura reaction of iodobenzene with phenylboronic acid (see text for the definition of FOM and details of the data set).

To evaluate the general applicability of our thin film catalyst we have explored the Suzuki–Miyaura reaction with iodo and bromobenzenes bearing various electron donating and withdrawing groups in different positions. Similar conditions as above were employed: ethanol solvent, K_2CO_3 base, 80 °C, and ambient atmosphere. The observations collected in Table 3 show that the catalyst is very effective in all cases except with methoxy substituted bromobenzene. It does not work well with chlorobenzene and its derivatives. Preliminary studies suggest that our catalyst film works well in other C–C coupling reactions as well. Progress of the Heck and Sonogashira reactions of styrene and phenylacetylene with iodo and bromobenzenes yielding stilbene and diphenylacetylene, respectively, catalyzed by our film is shown in Figure 8. These observations point to the feasibility of extending the application of the nanocomposite thin film catalyst to a number of organic transformations.

Table 3. Time Required for 100% Conversion in the Reaction of Phenylboronic Acid with Different Aryl Halides[a] in Ethanol Using K_2CO_3 as the Base and the Thin Film Catalyst (Pd-PVA layer, x = 0.13)[b]

X	R	time (h)
I	H	1.5
I	4-$COCH_3$	1.5
I	4-NO_2	1.5
I	4-NH_2	1.5
I	4-CH_3	1.5
I	4-OCH_3	2.0
I	2-OCH_3	3.5
Br	H	2.5
Br	4-$COCH_3$	2.5
Br	4-NO_2	2.5
Br	4-NH_2	3.0
Br	4-CH_3	3.5
Br	4-OCH_3	10.0
Br	2-OCH_3	20.0

[a] X = halogen; R = substituent on aromatic ring. [b] Reaction conditions: 1 mmol of aryl halide, 1.1 mmol of phenylboronic acid, 2 mmol of K_2CO_3, temperature = 80 °C.

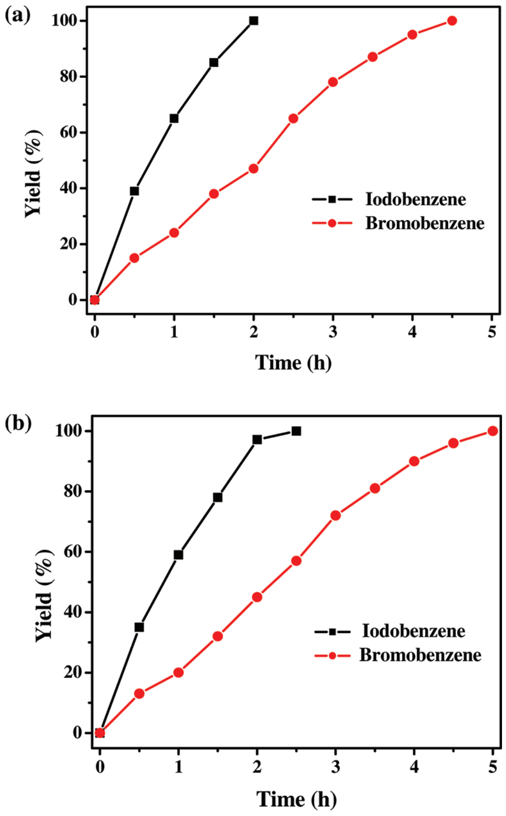

Figure 8. Progress of the (a) Heck reaction of styrene and (b) Sonogashira reaction of phenylacetylene, with iodo and bromobenzenes using ethanol as the solvent, K_2CO_3 as the base, and the thin film catalyst (Pd-PVA layer, x = 0.13); reaction conditions: 1 mmol of halobenzene, 1.1 mmol of styrene or phenylacetylene, 2 mmol of K_2CO_3, temperature = 80 °C.

■ CONCLUSIONS

We have developed a simple protocol for the fabrication of a multilayer Pd-PVA thin film using commercially available Pd precursor and aqueous medium for mixing with the polymer, and spin-coating/mild thermal annealing steps for the in situ generation of Pd nanoparticles inside the film. The thin film "dip catalyst" is gainfully employed in the Suzuki−Miyaura reaction of iodobenzene with phenylboronic acid, providing a very high yield, TON and TOF, and the possibility of scale up. Extensive recycling capability and the unique advantage of convenient catalyst monitoring between reuse cycles are demonstrated. A simple FOM is defined to integrate the various significant and quantifiable parameters related to the catalyst performance. An appraisal of the present catalyst in the context of the others reported in the recent literature is presented on the basis of the FOM. The "dip catalyst" with its ease and low cost of fabrication, convenience of deployment and recycling, and high catalytic efficiency is expected to be extremely useful in organic reactions of great synthetic utility.

■ ASSOCIATED CONTENT

Supporting Information

Details of catalyst film characterization and figure-of-merit estimation (11 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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