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Silica-supported palladium complex: An efficient, highly selective and reusable organic–inorganic hybrid catalyst for the synthesis of E-stilbenes

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ABSTRACT

A novel, highly efficient and reusable palladium based catalyst has been synthesized by covalent grafting of diphenyldiketone–monothiosemicarbazone on silica gel followed by metallation with palladium chloride, and the resulting organic–inorganic hybrid material was found to be highly effective catalyst for Suzuki-Miyaura cross-coupling reaction of various aryl halides with alkenyl boronic acid to give stilbenes. The catalyst was characterized by powder X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, energy dispersive X-ray fluorescence (ED-XRF), BET surface area analysis, solid-state ¹³C CPMAS NMR spectroscopy, atomic absorption spectroscopy (AAS), scanning electron microscopy (SEM) and elemental analysis. High turnover frequency, mild reaction conditions, high selectivity for E-stilbenes, and easy recovery and reusability of the catalyst renders the present protocol highly indispensable to address the industrial prerequisites and environmental concerns.

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1. Introduction

Palladium catalyzed Suzuki-Miyaura coupling reaction is among the most widespread and highly selective transformations for the synthesis of stilbenes, as these are the precursors for various biologically active compounds, pharmaceuticals, liquid crystalline materials, herbicides and conducting polymers. Over the past few decades, wide range of palladium based homogeneous catalysts have been used in this coupling reaction due to their high selectivity [1–9]. In addition, several homogeneous catalysts have been exploited for directing the stereochemistry of the reaction products. However, despite these benefits and advancement, homogeneous catalysis contributes only 20% in industrial processes due to various drawbacks such as use of large amount of catalyst, difficulty in purification of products and separation of soluble catalyst from the reaction mixture. Moreover, these homogeneous catalysts endow with the metal contamination of products which may be harmful for human health as well as for environment. Consequently, there is a huge demand for the innovation and development of novel catalysts with superior catalytic activities, lower costs, good recyclability and also less pollutive to the environment. In this regard, the development of

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heterogenized alternatives such as nanoparticle-supported, soluble polymer-supported and various organic/inorganic polymer supported catalysts has engrossed immense attention because they combine the advantages of both homogeneous and heterogeneous catalytic systems [10–16]. Among various inorganic supports for immobilizing palladium catalysts, silica is very promising because of its high surface area, good thermal stability, ready availability and economic viability, and relatively easy covalent modification with organic or organometallic moieties.

Similar to recoverable catalysts, microwave-promoted synthesis is also an area of escalating interest in both academic and industrial laboratories since microwaves are efficient and non-polluting mode of heating the reaction mixture [17-24]. So, the combination of microwave technology and heterogeneous catalysis is likely to have a great impact on sustainable chemistry, and proved to be a better catalytic system from both economic and environmental view point. Recently, we have reported an optimized procedure for preconcentration, determination and on-line recovery of palladium using highly selective diphenyldiketone-monothiosemicarbazone modified silica gel [25]. Following these results, and in continuation of our work on synthesis of inorganic-organic hybrid materials, and their applications as metal scavengers, sensors, and catalysts for various organic transformations [26-32], in the present paper we investigated the catalytic activity of silica supported Pd(II)diphenyldiketone-monothiosemicarbazone (Pd-DKTS-APSG) for the synthesis of stilbenes in microwave reaction system.

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Scheme 1. Preparation of silica supported palladium catalyst (Pd-DKTS-APSG).

2. Experimental

2.1. Materials and reagents

3-APTES (98%), silica gel (60–100 mesh) and *trans*-phenylvinyl boronic acid were purchased from Sigma–Aldrich. Thiosemicarbazide, diphenyldiketone, and all other starting materials and reagents used in the reactions were obtained commercially from Spectrochem. Pvt. Ltd., India and used without purification. The diphenyldiketone–monothiosemicarbazone (DKTS) was prepared according to the reported procedure [33].

2.2. Characterizations

Solid-state ¹³C cross-polarization magic-angle spinning (CPMAS) NMR spectra were recorded on Bruker DSX-300 NMR spectrometer. Elemental analysis (CHN) was performed using Elementar Analysensysteme GmbH VarioEL V3.00 instrument. Powder XRD patterns were recorded on Bruker D8 ADVANCE X-ray diffractometer using graphite monochromatized Cu-K α radiation. Surface area was calculated using the BET method on Gemini-V2.00 instrument (Micromeritics Instrument Corp.). Samples were outgassed at 100 °C for 3 h to evacuate the physically adsorbed moisture before measurement. Scanning electron microscopy (SEM) images were obtained using a ZEISS EVO 40 instrument. The samples were placed on a carbon tape and then coated with a thin layer of gold using a sputter coater. Qualitative analysis of catalyst for metal was performed using energy dispersive XRF spectrometer (Fischerscope X-ray XAN-FAD BC). The content of palladium in the catalyst was determined using LABINDIA AA 7000 atomic absorption spectrometer. The Fourier transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer spectrometer using KBr in the range of 4000–400 cm⁻¹. Catalytic reactions were carried out in Anton Paar multiwave 3000 microwave reaction system equipped with temperature and pressure sensor. The products obtained were analyzed and confirmed on an Agilent gas chromatography (6850 GC) using mass selective detector (5975 MSD).

2.3. Catalyst preparation

Firstly, the surface modification of silica gel was performed using a greener protocol [34] followed by grafting of diphenyldiketone–monothiosemicarbazone (DKTS) on aminopropylated silica gel (APSG) [25]. Then, the grafted silica gel, DKTS–APSG (1g) was refluxed with PdCl₂ (0.4 mmol) in acetone for 4 h. The dark brown solid was filtered off and washed thoroughly with acetone until the washings were colorless. The organic–inorganic hybrid catalyst (Pd–DKTS–APSG) thus obtained was dried in a vacuum oven (Scheme 1).

2.4. General procedure for Suzuki-Miyaura cross coupling reaction in microwave

A microwave vessel was charged with aryl halide (1 mmol), trans-2-phenylvinyl boronic acid (1.5 mmol), DMF-H₂O (3:2, 5 mL), K₂CO₃ (2.5 mmol) and catalyst (25 mg), and the whole reaction mixture was irradiated in microwave (120 W) at 110 °C for 25 min (Scheme 2). After the completion of reaction, the catalyst was filtered, and the reaction contents were subjected to multiple ethyl acetate extractions. The combined filtrates were washed with saturated sodium bicarbonate solution, and dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure, and the products obtained were analyzed and confirmed by GC-MS.

3. Results and discussion

3.1. Solid state ¹³C CPMAS NMR spectroscopy

The presence of 3-aminopropyl group after functionalization of silica gel with 3-APTES is confirmed by solid state ¹³C NMR spectroscopy. The ¹³C CPMAS NMR spectrum of APSG (Fig. 1a) shows the presence of three well resolved peaks at 9.44, 20.99 and 42.68 ppm assigned to the carbons of the propyl group which authenticate the synthesis of APSG [35]. The covalent linkage between the DKTS and the organic moiety on the silica can also be examined by ¹³C CPMAS



R=H, CH₃, OCH₃, COCH₃, CHO, NO₂

Scheme 2. Pd-DKTS-APSG catalyzed synthesis of E-stilbenes.



Fig. 1. ¹³C CPMAS NMR spectrum of (a) APSG and (b) Pd–DKTS–APSG.

NMR spectroscopy. In ¹³C CPMAS NMR spectrum of Pd–DKTS–APSG (Fig. 1b), in addition to three peaks of propyl group, new prominent peak appeared at 162 ppm which is assigned to carbon of C=N which clearly confirms the covalent grafting of palladium complex on APSG. Some small peaks in the range of 90–140 ppm and at 195 ppm are attributed to aromatic carbons and C=S, respectively.

3.2. Elemental and surface area analysis

BET surface area measurements were carried out to analyze the grafting reactions. The surface area of the bare silica was approximately 235.67 m² g⁻¹. The amine-functionalized silica (APSG) and immobilized complex (Pd-DKTS-APSG) showed a surface area of $152.04 \text{ m}^2 \text{ g}^{-1}$ and $69.66 \text{ m}^2 \text{ g}^{-1}$, respectively. In general, the anchoring of organic or organometallic moieties onto the silica matrix obstructs the access of nitrogen gas molecules, thus reducing its surface area. So, the reduction in surface area in the sequence SG > APSG > Pd-DKTS-APSG confirms the functionalization of silica gel with 3-aminopropyltriethoxy silane to give APSG, and its subsequent modification with DKTS and Pd(II) ions to yield the organic-inorganic hybrid catalyst (Pd-DKTS-APSG). The results of elemental analysis of APSG (nitrogen wt.% = 2.20, carbon wt.% = 6.60, hydrogen wt.% = 2.38) gives rise to the grafting capacity of 1.57 mmol g⁻¹, and C/N ratio was found to be \sim 3 which is close to the expected value thereby confirming the 3-APTES grafting on silica gel.

3.3. XRD studies

Small angle X-ray diffraction patterns of modified silica (APSG) and silica supported Pd catalyst are shown in Fig. 2. The observed pattern showed a broad peak at an angle $2\theta = 22^{\circ}$ which characterized the material with low crystallinity or the amorphous nature of silica. The slight decrease in intensity was observed in the XRD pattern of Pd–DKTS–APSG confirming the immobilization of DKTS ligand, and its further metallation with palladium. This decrease in intensity is attributed to the filling of the pores of silica surface on metallation or it may be due to reduction in X-ray scattering contrast between the channel wall of the silicate framework and ligand. The overall XRD pattern of the catalyst was found to be similar to modified silica gel, confirming that crystallinity of silica is maintained after modification reactions.



Fig. 2. XRD pattern of (a) APSG, (b) Pd–DKTS–APSG, and (c) reused Pd–DKTS–APSG.



Fig. 3. ED-XRF spectrum of silica supported palladium catalyst (Pd-DKTS-APSG).

3.4. ED-XRF and atomic absorption spectroscopy

To determine the metal loading of Pd–DKTS–APSG, the catalyst was digested in 10 mL of nitric acid in a microwave digester system for 10 min, and diluted sufficiently by double distilled water. The resulting solution was then subjected to AAS for metal analysis. The Pd content of the catalyst was found to be 0.7 wt.% of silica. Further to support the above observation, the catalyst was also subjected to energy dispersive X-rays fluorescence spectroscopy. The ED-XRF spectrum of catalyst (Pd–DKTS–APSG) is shown in Fig. 3, and the well resolved peak of palladium clearly confirms the presence of palladium in the catalyst.

3.5. SEM analysis

The morphology of the catalyst was characterized by scanning electron microscopy. SEM micrographs are presented at two different magnifications. SEM image at low magnification $(238 \times)$ (Fig. 4a) revealed that silica gel beads do not possess any cracks during the preparation of catalyst confirming its good mechanical strength. High magnification $(27.60 \times)$ SEM micrograph (Fig. 4b) depicted the uniform dispersion of palladium complex on the surface of silica which is responsible for its high activity.

3.6. Catalytic activity tests

The optimization of catalytic conditions was carried out employing the coupling of *trans*-2-phenylvinyl boronic acid with *p*-bromoanisole. *p*-Bromoanisole was chosen as the test substrate because it is electronically deactivated (+R-effect) toward oxidative addition of the catalyst, and gives accurate assessment of catalytic activity.

3.6.1. Effect of base and solvent

To examine the effect of base on the catalytic activity of Pd–DKTS–APSG, various bases (Et₃N, Na₂CO₃, K₂CO₃ and NaHCO₃) have been employed using series of solvents such as dioxane, toluene, H₂O, DMF, DMF–H₂O, and DCM (dichloromethane). Selected results are presented in (Fig. 5). It was found that present catalyst (Pd–DKTS–APSG) gave maximum conversion (96%) using K₂CO₃ as base in combination with polar solvent system, i.e. DMF–H₂O (may be due to the high solubility of the substrates in DMF–H₂O solvent system). As shown in Fig. 5, other combination of solvents/bases gave lower conversion.

3.6.2. Effect of temperature and time

To study the effect of temperature and time on the activity of the catalyst, model reaction was carried out at diverse range of temperatures (25-120 °C) for different intervals of time (5-25 min). The conversion of *p*-bromoanisole as a function of time and temperature is shown in Fig. 6. The results showed that at room temperature no change in the conversion of *p*-bromoanisole was observed even if the reaction was continued for 25 min. So, the temperature of the reaction was raised, and found that maximum conversion of *p*-bromoanisole was obtained when the reaction was carried out at 110 °C in microwave for 25 min.

3.6.3. Effect of mass of catalyst

The influence of catalyst mass on its activity was studied in the range of 5–30 mg of Pd–DKTS–APSG using *p*-bromoanisole and



Fig. 4. SEM image of Pd-DKT-APS at (a) low magnification (238×) and (b) high magnification (27.60×).



Fig. 5. Effect of base and solvent on conversion of *p*-bromoanisole (reaction conditions: *p*-bromoanisole (1 mmol), phenyl vinyl boronic acid (1.5 mmol), catalyst (25 mg), $110 \degree$ C in microwave (120 W) for 25 min).



Fig. 6. Effect of temperature and time on conversion of *p*-bromoanisole (reaction conditions: *p*-bromoanisole (1 mmol), phenyl vinyl boronic acid (1.5 mmol), catalyst (25 mg), K₂CO₃ (3 mmol), DMF–H₂O solvent, microwave (120 W)).

phenyl vinyl boronic acid in DMF-H₂O solvent system at $110 \degree C$ in microwave. The conversion and yield during each catalyst upload are shown in Table 1. When the catalyst mass was increased from 5 mg to 30 mg, the conversion of *p*-bromoanisole increased from 25

Table 1	
Effect of mass of catalyst on its activity. ^a	

Amount of catalyst/ (mg (mol%))	Conversion (%)	Yield (%)
Blank	-	-
5 (0.03)	25	22
10 (0.06)	45	41
15 (0.09)	70	68
20 (0.13)	95	88
25 (0.16)	96	91
30 (0.19)	96	91

^a Reaction conditions: *p*-bromoanisole (1 mmol), phenyl vinyl boronic acid (1.5 mmol), K_2CO_3 (3 mmol), DMF-H₂O solvent, 110 °C in microwave for 25 min.

to 96% and the selectivity reached 100%. This is because on increasing the amount of catalyst, number of active sites on the porous surface of catalyst has increased.

3.7. Pd–DKTS–APSG catalyzed Suzuki-Miyaura cross coupling reaction

In order to evaluate the scope of the present catalytic system, cross coupling of *trans*-phenylvinyl boronic acid with various aryl halides have been studied. The catalyst was able to activate the carbon halogen bond of both substituted and un-substituted aryl halides. In all the cases, E-stilbenes were formed depicting the high selectivity of the present catalytic system. Both electron deficient and electron rich aryl halides gave products in good yields with high turnover frequency (TOF) values (Table 2). The present catalytic system was also compared with some reported catalysts (Table 3) [36–40], and found that our organic–inorganic hybrid catalytic system (Pd–DKTS–APSG) is better than the reported ones in terms of yield, cost, reaction time, selectivity, turn over frequency and reusability.

3.8. Plausible reaction mechanism

The proposed catalytic route is shown in Scheme 3. It is very well known that in addition to nature of substrate, cross coupling reaction is sensitive to both steric and electronic properties of the catalyst. The present catalytic system (Pd–DKTS–APSG) was found to be highly effective for activating the carbon halogen bond of both substituted and un-substituted aryl halides to give E-stilbenes. This outstanding activity and selectivity of the catalyst has been attributed to the electronic properties of the DKTS ligand (σ donation by N and S atoms) which stabilizes the palladium in +2 oxidation state. In addition, steric properties of the DKTS ligand (two bulky aryl groups) helps in reductive elimination step, and hence maintained the stereoselectivity of the product.

3.9. Heterogeneity test

To confirm the heterogeneous nature of the catalyst, the filtration test was applied. During the reaction, catalyst was separated from the reaction mixture by filtration (after 15 min). The filtrate was allowed to react for additional 5–6 min and no increment in conversion was observed. This confirms that the reaction did not proceed after the removal of the catalyst. After the completion of reaction, the liquid phase of the reaction mixture was collected by filtration and tested with atomic absorption spectrophotometer. Absence of palladium in the reaction mixture suggested that no leaching of the catalyst was observed during the reaction.

3.10. Recycling of catalyst

After the completion of reaction, the catalyst was recovered simply by filtration and then washed properly with DMF, water and chloroform. The recovered catalyst was dried under vacuum oven at 100 °C, and then used again in successive cycles (six) under identical reaction conditions (Table 4). The results showed that there is no appreciable loss of catalytic activity. Comparison of IR and XRD spectra of fresh and recovered catalysts suggests that the structural properties of recycled catalyst remained unaltered after the reaction as none of the vibrations change significantly. The catalyst was recovered, recycled, and used for 6 consecutive trials without the loss of its activity and selectivity.

 Table 2

 Pd-DKTS-APSG catalyzed Suzuki cross coupling reaction of aryl halides with *trans*-phenylvinyl boronic acid.^a

Entry	Aryl halide	Product	Conv. ^b (%)	Yield ^b (%)	TOF ^c (h ⁻¹)
1			100	95	1404
2	Br		96	92	1360
3	CI		90	81	1197
4	H ₃ C Br		94	88	1300
5	H ₃ CO Br	OCH3	96	91	1345



^a Reaction conditions: aryl halide (1 mmol), phenyl vinyl boronic acid (1.5 mmol), K₂CO₃ (3 mmol), catalyst (25 mg), DMF-H₂O solvent, 110 °C in microwave for 25 min. ^b Conversion and yield were determined by GC.

^c TOF (turn over frequency) = number of moles of aryl halide converted in to product/mol of active site/time.

Table 3

Literature precedents for the synthesis of stilbenes.

Entry	Aryl halide	Catalytic system	Reaction conditions	Yield (%)	Ref.
1	Br	Pd(dba)3 (dba-dibenzylidene acetone)	Aryl vinyl iodide, 70 °C, 3 h, THF solvent.	78	[36]
2	Br	Palladium acetate	Trans-phenylvinyl boronic acid, 150 °C, 5 min, H2O–TBAB, Na2CO3	91	[37]
3	Br OCH3	Palladium-N-heterocyclic carbene complex	Trans-phenylvinyl boronic acid, 80°C, 24h, dioxane solvent	85	[38]
4	Br OCH3	2.5 ppm Pd	trans-phenylvinyl boronic acid, 150 °C, 5 min., H ₂ O–TBAB, Na ₂ CO ₃	46	[37]
5	Br CHO	[Pd(C ₃ H ₅)Cl] ₂ and tetrapodal phosphane ligand	Trans-phenylvinyl boronic acid, 20 h Xylene, 130 °C, K2CO3	100	[39]
6	Br H ₃ C	2.5 ppm Pd	Trans-phenylvinyl boronic acid, 150 °C, 5 min, H2O-TBAB, Na2CO3	26	[37]
7	Br CH ₃	Pd(dba) ₃	Aryl vinyl iodide, 70 °C, 5 h, THF solvent.	72	[36]
8	Br CH ₃	Pd(OAc) ₂	Trans-phenylvinyl boronic acid, 150 °C, 5 min, H ₂ O/EtOH/TBAB, Na ₂ CO ₃	91	[37]
9	Br COCH3	2.5 ppm Pd	Trans-phenylvinyl boronic acid, 150 °C, 5 min, H2O–TBAB, Na2CO3	89	[37]
10	Br — COCH3	$[Pd(C_3H_5)Cl]_2$ and tetrapodal phosphane ligand	Trans-phenylvinyl boronic acid, 20 h Xylene, 130 °C, K₂CO₃	80	[39]
11	CI	Pd(dba)3 (dba-dibenzylidene acetone) and benzoferrocene	Trans-phenylvinyl boronic acid, 24 h, 1,4-dioxane, Cs ₂ CO ₃	90	[40]

Table 4 Recycling of the catalyst.^a

Cycle	Conversion (%)	Yield (%)	$TOF(h^{-1})$	
1	96	91	1345	
2	96	91	1345	
3	96	91	1345	
4	95	90	1330	
5	95	90	1330	
6	94	89	1315	

^a Reaction conditions: p-bromoanisole (1 mmol), phenyl vinyl boronic acid (1.5 mmol), K₂CO₃ (3 mmol), catalyst (25 mg), DMF-H₂O solvent, 110 °C in microwave for 25 min.





Scheme 3. Proposed reaction mechanisms.

4. Conclusion

We have developed a novel, efficient and reusable silica based organic-inorganic hybrid palladium-catalyst (Pd-DKTS-APSG) for Suzuki-Miyaura cross-coupling reaction to yield E-stilbenes. The supported catalyst displayed good activity and selectivity at low Pd loading (0.7 wt.%). The supported catalyst could be easily separated and recovered from the reaction mixture (by simple filtration) and reused several times. The combination of advantages displayed by the Pd-DKTS-APSG catalytic system such as: economic viability, easy preparation, high catalytic activity, stability, reusability, and no measurable Pd leaching, prove that the present catalyst should be considered as a viable alternative in cross-coupling reactions on efficiency, environmental concerns and economical grounds.

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