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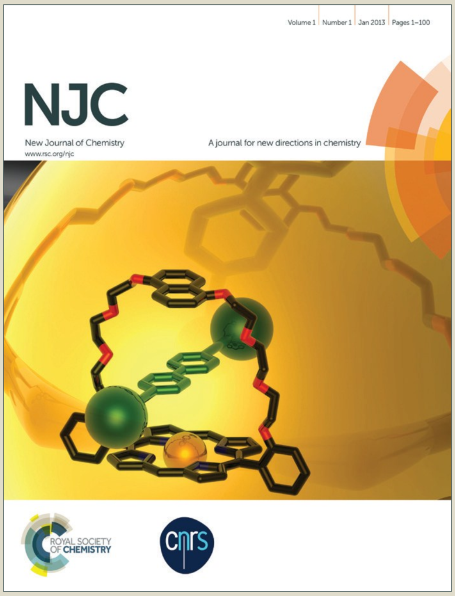

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ARTICLE

A simple, phosphine free, reusable Pd(II)-2,2'-Dihydroxybenzo phenone-SBA-15 catalyst for arylation and hydrogenation reactions of alkenes

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An efficient, simple, phosphine and co-catalyst free C-C coupling reaction heterogeneous catalyst via. post grafting method is developed and reported. Covalently anchored phosphine free Pd(II) based 2,2'-dihydroxybenzophenone (DHBP) complex over organofunctionalized SBA-15 has been synthesized by the reaction between aminofunctionalized SBA-15 (NH_2SBA-15) and 2,2'-dihydroxybenzophenone (DHBP) ligand, and further complexation with Pd(II)Cl_2 to get Pd(II)-DHBP@SBA-15. The synthesized catalysts were characterized by elemental analysis, XRD, N_2 sorption analyses, TG, DTA, FT-IR, solid state ^{13}C and ^{29}Si NMR spectra, XPS, UV-Visible, SEM, EDAX and TEM. The synthesized catalysts were screened in arylation (Heck reactions) and hydrogenation reactions of alkenes, and the results show that Pd(II)-DHBP@SBA-15 exhibits high conversion and selectivity towards arylation and hydrogenation reactions of alkenes with high stability. The anchored solid catalysts can be recycled effectively and reused several times without major loss in activity.

Introduction

The discovery of C-C coupling reactions in 19th century has opened up several alternative challenges for the production of fine chemicals. A lot of materials such as ionic liquids,[1] silica supported[2] and polymer supported[3] catalysts, pure Pd/C[4] etc were used for the carbon-carbon coupling reactions. The phosphine supported catalysts[5] for C-C coupling reactions are well established method in the past decades. However, several drawbacks of phosphine ligands such as cost, toxicity and recovery from the reaction mixture are challenging and has resulted in the process being less preferred. In addition, phosphine undergoes oxidation in catalytic cycle to get phosphine oxide, and thereby causing the cleavage of P-C bond and degradation of the catalytic cycle. Due to these reason, there is a growing interest in the development of phosphine free heterogeneous catalyst.[6] Such a catalyst should be stable under ambient conditions and should afford coupling products in high yields at short reaction times. Out of carbon-carbon cross-coupling reactions, the arylation of alkenes[7] in the presence of a base (Heck reaction) is an excellent method for the synthesis of fine chemicals.

In the past decades, complexes of palladium such as palladium acetate, palladium chloride or triarylphosphine palladium complexes are used[8] in the arylation reactions of alkenes with aryl halides. However, as with all homogeneous catalysts, its separation and reusability are difficult, thereby increasing the production cost with liberation of large volumes of hazardous wastes. To mitigate the above mentioned serious problems, palladium based organofunctionalized mesoporous catalysts,[9-11] which shows high periodicity in the pore arrangement as well as high surface area and pore sizes, have been synthesized *via.* post grafting method and used for coupling reactions.[12] Further, liquid phase hydrogenation of alkenes[13,14] using heterogeneous catalysts are relevant industrial process to obtain alkanes. An appropriate, cheap and simple ligand is necessary for synthesis of highly active palladium based organofunctionalized complexes. For this purpose, a number of ligands such as C-N based and N,N' based ligands[15] have been reported for coupling reactions. Due to the instability and tedious synthesis procedure of previously said ligands, a robust and stable 2,2'-Dihydroxy benzophenone ligand derivative is used in the present study.

To heterogenize the palladium based organofunctionalized complexes with better stability and to avoid the diffusional strain of reactants in the channels of other mesoporous or microporous materials, solid support like SBA-15 is synthesized by using neutral triblock polyether as templates and TEOS as silica precursor. In addition, SBA-15[16] has the advantage due to its special characteristics such as high surface area, uniform pore sizes, high wall thickness and high hydrothermal stability compared to other mesoporous materials like MCM-41, MCM-48. To explore the utility of SBA-15 materials, especially in catalysis, the surface of SBA-15 was modified by organic functional groups for anchoring of metals and metal complexes.[17]

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In this work, we tried to synthesize and characterize highly efficient, phosphine and co-catalyst free, reusable heterogeneous catalyst, Pd(II)-DHBP@SBA-15 for arylation and hydrogenation reactions of alkenes. Synthesis of Pd(II)-DHBP@SBA-15 catalyst mainly divided into four steps and it is described as (i) synthesis of parent solid support like SBA-15 (ii) aminofunctionalization of SBA-15 (iii) anchoring of 2,2'-dihydroxybenzopheneone (DHBP) ligand over amino-functionalized SBA-15 (NH_2SBA-15) and (iv) metallation of heterogenized ligand (DHBP@SBA-15) with $Pd(II)Cl_2$.

Experimental

Synthesis of Pd(II)-DHBP@SBA-15

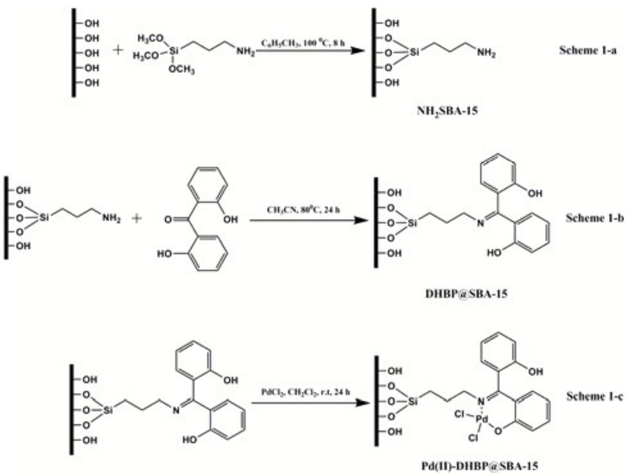
Pluronic 123 (P123, Average MolWt = 5800), tetraethylorthosilicate (TEOS), 3-aminopropyltrimethoxysilane (3-APTMS), 2,2'-dihydroxybenzophenone (DHBP) and $Pd(II)Cl_2$ were purchased from Aldrich. In addition, aryl halides and alkenes as organic reagents used for the coupling and hydrogenation reactions were purchased from Aldrich. Further, hydrochloric acid (HCl) and solvents like dichloromethane (DCM), acetonitrile (CH3CN) and toluene were purchased from Merck. All chemicals were used as received without further purification.

The synthesis of SBA-15 was carried out by using modified literature procedure with the following initial molar gel compositions : [18]

0.043 TEOS: 4.4g P123 Mavg = 5800 [EO_{20}-PO_{70}-EO_{20}]: 8.33 H_2O: 0.24 HCl

Typically, Pluorinc123 called as P_{123} (4.4 g), a triblock co-polymer consider as surfactant, was dispersed in 30 g distilled water and stirred for 1.5 h. 120 g of 2 M HCl was added into the above solutions with constant stirring and stirring was continued for next 2 h. Eventually, 9 g of TEOS as silica presursor was added drop wise and the resulting solution was maintained at 35 °C for 24 h with stirring. The resulted heterogeneous mixture was submitted to hydrothermal treatment at 100°C for 48 h under static condition. The solid product was filtered, washed with distilled water and dried in oven at 70°C for 12 h, and then calcined at 540 °C for 8 h in air to get calcined SBA-15. [18]

The aminofunctionalized SBA-15 (NH_2SBA-15) was synthesized by using 3-aminopropyltrimethoxysilane (3-APTMS) as organic linker via. Post-grafting method (scheme 1-a). The reaction procedure briefly explained as: 3 g of calcined SBA-15 was dispersed in 60 ml dry toluene followed by 1.5 g of 3-APTMS was added into this solution under N_2 atmosphere and the reaction mixture was refluxed at 100 °C for 8 h. The solid material was filtered, washed with toluene and dichloromethane, and dried in oven at 70 °C for 12 h. The dried material was extracted by Soxhlet apparatus with dichloromethane as solvent to remove the unreacted silylating agent like 3-APTMS and was vacuum dried at 473K to get NH_2SBA-15.



Scheme 1: Organofunctionalization and heterogenization of 2,2'-Dihydroxybenzophenone (DHBP) complex over SBA-15 [Pd(II)-DHBP@SBA-15], 1-a: Aminofunctionalization of SBA-15 [NH_2SBA-15], 1-b: Immobilization of 2,2'-Dihydroxybenzophenone Ligand (DHBP) over NH_2SBA-15 [DHBP@SBA-15], 1-c: Complexation of heterogenized ligand [Pd(II)-DHBP@SBA-15].

The synthesis of Pd(II)-DHBP@SBA-15 is mainly divided into two steps as shortly described as (i) anchoring of 2,2'-dihydroxybenzophenone ligand (DHBP) over amino-functionalized SBA-15 (NH_2SBA-15) (scheme 1-b) to get DHBP@SBA-15 and (ii) complexation of heterogenized ligand (DHBP@SBA-15) with $Pd(II)Cl_2$ to achieve Pd(II)-DHBP@SBA-15 (scheme 1-c). In briefly, the first step involves the addition of 2,2'-dihydroxybenzophenone (0.52 g, 2.41 mmol) which is dissolved in 35 ml of dry acetonitrile into the dispersed solutions of NH_2SBA-15 (1 g) in 15 ml of dry acetonitrile. The reaction mixture was refluxed at 70 °C for 24 h with constant stirring, and then filtered, washed thoroughly with acetonitrile and dried in oven at 50 °C for 16 h to get DHBP@SBA-15 (scheme 1-b) . In second step, called as metallation process, 0.2 g of $Pd(II)Cl_2$ (1.13 mmol) in 20 ml of dichloromethane was added into the solution of heterogenized ligand, DHBP@SBA-15 (1 g) in 10 ml of dichloromethane. The dispersed solutions was stirred at room temperature for 24 h, and then filtered, washed with dichloromethane and dried in oven at 50 °C for 12 h. The dried material was Soxhlet extracted with dichloromethane to remove unreacted $Pd(II)Cl_2$ to attain Pd(II)-DHBP@SBA-15 (scheme 1-c).

The arylation of alkenes under palladium catalysts is one of the important organic reactions, referred as Heck reaction, which is helpful for the synthesis of various types of coupling compounds. Arylations of alkenes were carried out in a 50 ml double necked RB flask fitted with a water-cooled condenser and magnetic stirrer by using Et_3N as base. In typical Heck reaction procedure, a mixture of 0.015 g of Pd(II)-DHBP@SBA-15, aryl halide (1 mmol), alkenes (1.2 mmol), Et_3N (3.5 mmol) and 3.5 ml of DMF was refluxed at 120 °C for 12 h. The samples were withdrawn periodically and cooled sample was analyzed using a Gas chromatography (HP, Agilent 68909 N) equipped with a capillary column (HP-5) and FID detector.

Hydrogenation reactions of alkenes, especially aromatic olefins, cycloolefins, aliphatic olefins and bicyclo olefins are used to synthesize various hydrocarbons, which can be applied in industrial chemistry. In a typical procedure, a mixture of 0.015 g of Pd(II)-DHBP@SBA-15 and olefins (5 mmol) in 50 ml

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methanol were taken in 100 ml Parr autoclave reactor and stirred with H_2 Pressure (5 bar) at room temperature for 15 minutes. The samples were withdrawn periodically and cooled sample was analyzed using a Gas chromatography (HP, Agilent 68909 N) equipped with a capillary column (HP-5) and FID detector.

Elemental analysis (C, H and N) was performed on a Carlo Erba (Model EA 1108) elemental analyzer. The palladium metal content in the material was determined by EDAX analysis using a dual beam scanning electron microscope (FEI company, model Quanta 200 3D) operating at 30 kV. Powder X-ray diffraction (XRD) patterns were measured on a PAN analytical X'pert Pro dual goniometer diffractometer using Ni-filtered CuKα radiation (λ = 1.5404 Å) over the range 0.5 – 5 ° (SAXRD). N2 adsorption–desorption isotherms, pore size distributions as well as the textural properties of the hybrid materials were determined by using a Autosorb 1C Quantachrome USA. The program consisting of both an adsorption and desorption branch and typically ran at -196 °C after samples were degassed at 150 °C for 4 h. The BET method was applied to calculate the total surface area at relative pressures of P/Po = 0.65–0.45 and the BJH model applied to the adsorption branch of the isotherm to determine the total pore volume and average pore diameter at a relative pressure of P/Po = 0.99. Pore size distribution curves were obtained via the NLDFT model assuming cylindrical pore geometry. FTIR spectra of the solid samples were recorded in the range of 4000–400 cm-1 on a Bruker alpha T FTIR spectrophotometer under room temperatures. Magic angle spinning (MAS) NMR spectra for 29Si and 13C nuclei were recorded on BRUKER DSX300 spectrometer at 7.05 T (resonance frequencies 59.595 MHz, rotor speed 10000 Hz and 75.43 MHz, rotor speed 10000 Hz). XPS measurements were performed on a VG Microtech ESCA 3000 instrument, using monochromatized MgKα radiation at pass energy of 50 eV and an electron take off angle of 60 °. DR UV-Vis spectra of thecomplexes were analyzed by using a Perkin-Elmer model Lambda 650 spectrophotometer.The scanning electron micrographs of the samples were obtained in dual beam scanning electron microscope (FEI company, model Quanta 200 3D) operating at 30 kV. The samples were loaded on stubs and sputtered with thin gold film to prevent surface charging and also to protect from thermal damage due to electron beam. A JEOL JEM-3010 and Tecnai (Model F30) both operating at 300 kV were used for HRTEM samples observation. Samples were crushed and dispersed in isopropanol with low power sonication before putting a drop over carbon coated Cu grid for observation.

Results and discussion

Characterization of Pd(II)-DHBP@SBA-15

The synthesized catalysts were characterized by different physico-chemical characterization techniques and the results are discussed below. The XRD pattern of (a) as-synthesized SBA-15 (b) calcined SBA-15 (c) NH_2SBA-15 and (d) Pd(II)-DHBP@SBA-15 are represented in Fig. 1. The uniqueness of mesoporous structure, phase purity, degree of orderdness and unit cell parameters of all synthesized catalysts were determined by powder X-ray diffraction. The typical hexagonal phase (p6mm) of SBA-15 showing three reflections, mainly (100) peak with weak (110) and (200) peaks are clearly visible in all samples at 2θ = 0.90°, 1.50° and 1.74°, respectively. This indicates high degree of orderedness of the two dimensional hexagonal mesophase.[19] In all the synthesized catalysts [Fig. 1(a-d)], (110) reflection is more intense than (200) reflection, which occurs due to the complete condensation of the wall structure owing to the higher hydrothermal synthesis temperature at calcination. Further, the XRD pattern of calcined SBA-15 [Fig. 1(b)] shows intense peak compared with the as-synthesized SBA-15 which reveals that surfactant present in as-synthesized sample was completely removed from calcined SBA-15. The peak intensities of (100) reflections in NH_2SBA-15 and Pd(II)-DHBP@SBA-15 [Fig. 1(c,d)] were gradually decreasing from calcined SBA-15 due to the proper loading of organic modifier and homogeneous complexes, respectively, on calcined SBA-15.

The physical properties of calcined SBA-15 and Pd(II)-DHBP@SBA-15 are summarized in Table 1. The BET surface area, pore volume, pore diameter, unit cell parameter and pore wall thickness of calcined SBA-15 and Pd(II)-DHBP@SBA-15 are found to be 550 m^2/g, 1.02 cc/g, 65.00 Å, 102.54 Å , 36.54 Å and 220 m^2/g, 0.51 cc/g, 47.00 Å, 103.00 Å, 55.00 Å, respectively. As shown in Table 1, compared to SBA-15, a further reduction of surface area, pore volume and pore diameter were observed in Pd(II)-DHBP@SBA-15 catalyst, indicating the successful anchoring of homogeneous complex on the channels of SBA-15. The N_2 adsorption-desorption isotherm and pore size distribution curves (inset) of (a) calcined SBA-15 and (b) Pd(II)-DHBP@SBA-15 are plotted in Fig. 2. In both materials, calcined SBA-15 and Pd(II)-DHBP@SBA-15, exhibit type IV type isotherm with H1 hysteresis loop related to capillary condensation step, a characteristic feature of the highly ordered mesoporous materials (2-50 nm).[20]

The weight percentage of organomoities on SBA-15 and the thermal stability of (a) as-synthesized SBA-15 (b) calcined SBA-15 (c) NH_2SBA-15 and (d) Pd(II)-DHBP@SBA-15 were determined by TGA (Fig. 3A) and DTA (Fig. 3B) in an atmosphere of air from 30 to 1000 °C with a temperature ramp of 10 °C min^{-1}. As-syntheiszed SBA-15 [Fig. 3A(a)] exhibits a 50 % weight loss in TG analysis with observation of an exothermic peak in DTA analysis [Fig. 3B(a)], in the range of 175 °C to 230 °C. This it can be inferred that the decomposition of surfactants present in as-synthesized SBA-15. In calcined SBA-15[Fig. 3A(b)], a 11 % weight loss was observed in TGA due to the physisorbed water molecules, and no peak was observed in DTA analysis [Fig. 3B(b)]. This indicates a complete removal of surfactants from parent SBA-15 with the generation of pure siliceous material. The TG and DTA analyses of NH_2SBA-15 [Fig. 3A &B(c)] shows two distinct weight loss regions; first one, corresponds to adsorbed moisture molecule in the region of 75 °C to 150 °C and second one, indicates to

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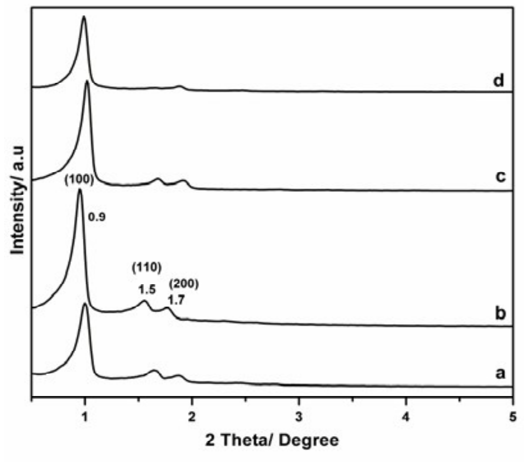

Fig. 1: XRD pattern of (a) as-synthesized SBA-15 (b) calcined SBA-15 (c) NH_2SBA-15 and (d) Pd(II)-DHBP@SBA-15.

Table 1: Textural properties[a] of SBA-15 and Pd(II)-DHBP@SBA-15.

Sample	a_0[b] [Å]	SA [m^2/g]	Dp [Å]	Vp [cc/g]	ωt[c] (Å)
SBA-15	102.54	550	65	1.02	36.54
Pd(II)-DHBP @SBA-15	103.00	220	47	0.51	55.00

[a] a_0, Unit Cell parameter; SA, BET Surface Area; Dp, Pore Diameter; Vp, Pore Volume; ω_t, Wall Thickness; Pd content=6.88 Wt% (EDAX); b $a_0=2d_{100}/1.73$; c $\omega_t = a_0$-Dp.

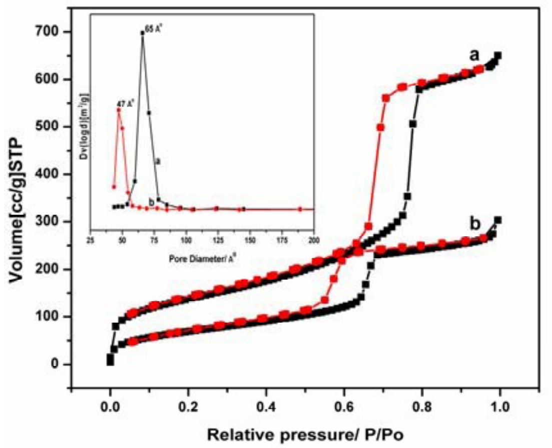

Fig. 2: N_2 adsorption-desorption isotherms and pore size distribution curves (inset) of (a) calcined SBA-15 and (b) Pd(II)-DHBP@SBA-15.

the decomposition of aminopropyl moiety from NH_2SBA-15 in the range of 250 °C to 320 °C. In the case of Pd(II)-DHBP@SBA-15 [Fig. 3A &B(d)], an extra peak was observed between 350 °C and 420 °C along with the peaks for aminopropyl group in NH_2SBA-15. The combustion of Pd(II)-2,2'-dihydroxy benzophenone (DHBP) complex can be confirmed along with the high thermal stability of organomoities on SBA-15. The

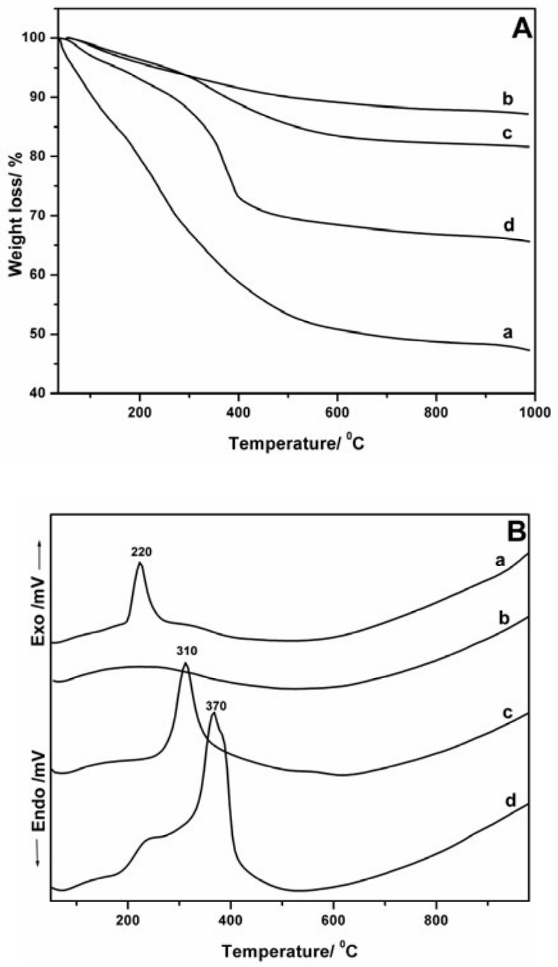

Fig. 3: TGA (A) and DTA (B) pattern of (a) as-synthesized SBA-15 (b) calcined SBA-15 (c) NH_2SBA-15 and (d) Pd(II)-DHBP@SBA-15.

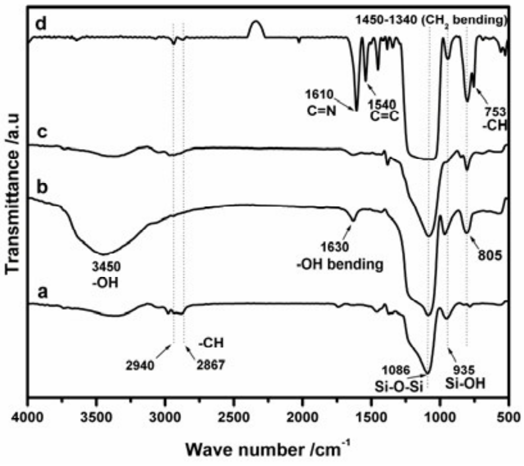

Fig. 4: FT-IR spectroscopy of (a) as-synthesized SBA-15 (b) calcined SBA-15 (c) NH_2SBA-15 and (d) Pd(II)-DHBP@SBA-15.

TGA results of NH_2SBA-15 [Fig. 3A(c)] exhibits 18 % weight loss which is greater than calcined SBA-15 (11 %) [Fig. 3A(b)] indicating the successful anchoring of 3-APTMS on the calcined

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SBA-15. Further, Pd(II)-DHBP@SBA-15 [Fig. 3A(d)] shows 31 % of weight loss, being greater than the loss observed for the NH$_2$SBA-15, strongly supporting a 13 % loading of neat Pd(II)-2,2'-dihydroxy benzophenone (DHBP) complex on calcined SBA-15. All decomposition results of synthesized materials from TG and DTA analyses confirms that the successful anchoring of organo-modifier and neat homogeneous complex over SBA-15.

DRIFTS was employed to find out the nature of surface silanol groups and organomoities attached on SBA-15. The FT-IR spectra of (a) as-synthesized SBA-15 (b) calcined SBA-15 (c) NH$_2$SBA-15 and (d) Pd(II)-DHBP@SBA-15 are depicted in Fig. 4. The peaks at 2940 and 2867 cm^{-1} in the as-synthesized SBA-15 [Fig. 4(a)] are attributed to the -CH$_2$ asymmetrical and symmetrical stretching vibrations of surfactant molecules present in host materials. After calcination, [Fig. 4(b)] the above mentioned peaks disappeared due to the complete removal of surfactants, and a broad band at 3800-3000 cm^{-1} and a medium sharp band at 1630 cm^{-1} were observed, which corresponds to -OH stretching and bending vibrations of isolated surface silanol groups in calcined SBA-15.[21,22] After aminofunctionalization, NH$_2$SBA-15 [Fig. 4(c)], the peaks at 2940 and 2867 cm^{-1} due to the stretching vibrations of –CH$_2$ groups [17] in propyl chain of 3-APTMS indicating the successful anchoring of organic linker on parent SBA-15. Further, the peaks at ~3300 cm^{-1} and ~1500 cm^{-1} correspond to stretching and bending vibrations of N-H bond [15] in NH$_2$SBA-15 [Fig. 4(c)]. In the case of Pd(II)-DHBP@SBA-15 [Fig. 4(d)], an additional peaks at 753 cm^{-1} and 1540 cm^{-1} are assigned to C–H bending and C=C stretching vibrations,[18] respectively, of the arene groups. Moreover, a strong band at 1610 cm^{-1} is assigned to the –C=N stretching vibration of the azomethylene group.[18] In addition, well pronounced band at 1450 to 1340 cm^{-1} correspond to the –CH$_2$ bending vibrations [17] of propyl chain in Pd(II)-DHBP@SBA-15. The spectrum of as-synthesized SBA-15, calcined SBA-15, NH$_2$SBA-15 and Pd(II)-DHBP@SBA-15 [Fig. 4(a-d)] exhibit the bands at 1086 cm^{-1} and 805 cm^{-1} assigned to the asymmetric and symmetric stretching vibrations of Si-O bond in Si-O-Si and a strong band at 935 cm^{-1} is attributed to v(Si–OH) vibrations in silica framework.[23,24] The results from FT-IR spectra indicates successfully anchoring of neat Pd(II)-2,2'-dihydroxy benzophenone (DHBP) complex into parent SBA-15.

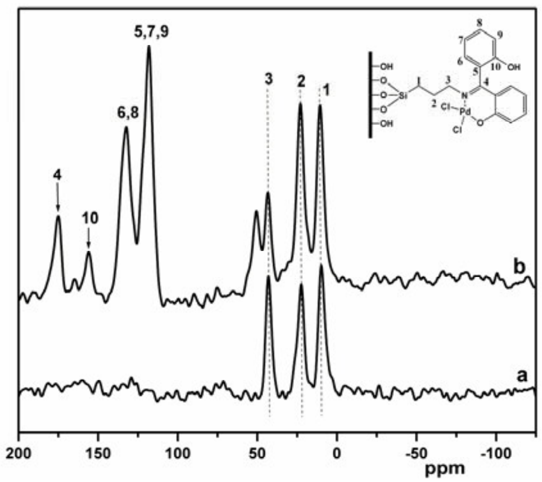

Fig. 5: Solid state ^{13}C NMR spectroscopy of (a) NH$_2$SBA-15 and (b) Pd(II)-DHBP@SBA-15.

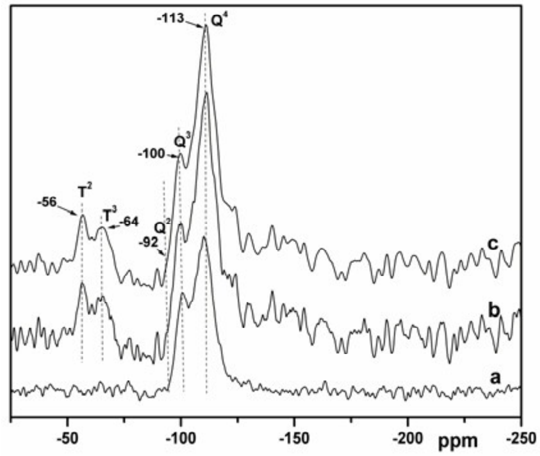

Fig. 6: Solid state ^{29}Si NMR spectroscopy of (A) calcined SBA-15 (B) NH$_2$SBA-15 and (C) Pd(II)-DHBP@SBA-15.

The ^{13}C solid state NMR spectra of (a) NH$_2$SBA-15 and (b) Pd(II)-DHBP@SBA-15 are plotted in Fig. 5. In aminofunctionalized SBA-15 [Fig. 5(a)], peaks at 10, 23 and 43 ppm corresponds to the carbon atoms of propyl chain in organic modifier, indicating the successful aminofunctionalization of SBA-15. In the case of Pd(II)-DHBP@SBA-15 catalyst [Fig. 5(b)], peaks in the range of 110-145 ppm, assigned to aromatic carbon atoms of 2,2'-dihydroxybenzophenone (DHBP) ligand, which is anchored over aminofunctionalized SBA-15. In addition, peaks at 156 ppm and 176 ppm are ascribed to –CH(OH) group in aromatic ring and azomethine (-C=N) group in Pd(II)-DHBP@SBA-15 catalyst, respectively. All resonance peaks related with organomoities confirm the anchoring of Pd(II)-2,2'-dihydroxybenzophenone (DHBP) sites on SBA-15. The ^{29}Si CP-MAS NMR spectroscopy has been employed to find out the degree of functionalization of surface silanol groups with organic moieties on the mesostructured materials. ^{29}Si solid state NMR spectra of (a) calcined SBA-15 (b) NH$_2$SBA-15 and (c) Pd(II)-DHBP@SBA-15 are represented in Fig. 6. A broad resonance peaks from -90 to -110 ppm are assigned to Si–O–Si and Si–OH bonds in all synthesized catalysts [Fig. 6(a-c)]. The peaks at -92 ppm, -100 ppm and -110 ppm are corresponds to the Q^2 [geminal silanol, (SiO)$_2$Si(OH)$_2$], Q^3 [single silanol, (SiO)$_3$Si(OH)] and Q^4 [siloxane, (SiO)$_4$Si] sites of the silica framework, respectively.[21,22] The spectra of NH$_2$SBA-15 [Fig. 6(b)] and Pd(II)-DHBP@SBA-15 [Fig. 6(c)] exhibit two additional peaks at -64 ppm and -56 ppm assigned to T^3 [SiR(OSi)$_3$] and T^2 [Si(OH)R(OSi)$_2$] units, respectively which is conspicuously absent in parent SBA-15. The presence of T^3 and T^2 signals confirm that SBA-15 has been modified by organomoeities. In addition, aminofunctionalized SBA-15 shows a decrease in Q^2

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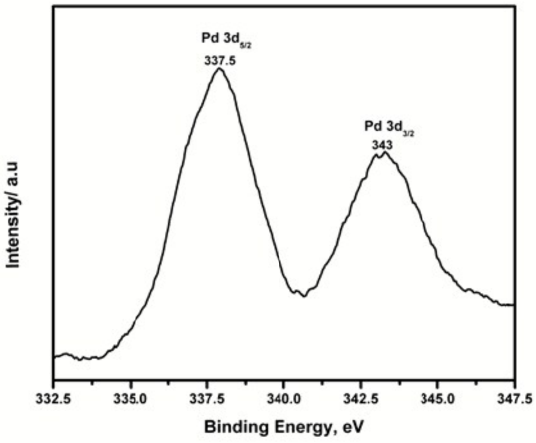

Fig. 7: XPS spectroscopy of $3d_{5/2}$ and $3d_{3/2}$ core levels of Pd(II)-DHBP@SBA-15.

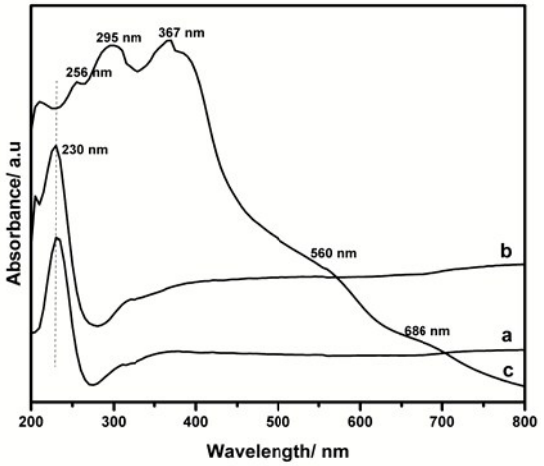

Fig. 8: DR UV-Vis spectroscopy of (a) calcined SBA-15 (b) NH_2SBA-15 and (c) Pd(II)-DHBP@SBA-15.

and Q^3 sites with the increase of Q^4 site, compared to calcined SBA-15, indicating the effective consumption of the geminal as well as isolated silanol sites by using 3-APTMS as organic modifier. The results from ^{29}Si NMR spectra confirm a highly condensed siloxane network with organic group covalently bound to the mesoporous silica and the stability of Si-C bond in Pd(II)-DHBP@SBA-15 catalyst.

X-ray Photoelectron Spectroscopy and DR UV-Visible spectroscopy can be used to find out the oxidation state and chemical environment of synthesized catalysts. The XPS spectra of Pd 3d core levels of Pd(II)-DHBP@SBA-15 is plotted in Fig. 7. All the spectra were calibrated and charge corrected to C1s peak of carbon at 284.6 eV as standard reference. The peaks at 337.5 eV and 343 eV in Pd(II)-DHBP@SBA-15 catalyst corresponds to Pd$3d_{5/2}$ and Pd$3d_{3/2}$ spin orbit component, indicating that palladium exists in +2 oxidation state. In addition, the XPS spectra of spent catalyst was shown in Fig. S1 [ESI †]. The 3d5/2 and 3d3/2 core levels of spent catalyst were observed at 335.7 eV and 340.8 eV, respectively, indicating the palladium exists as Pd(0) state, which is stabilized by phenolic

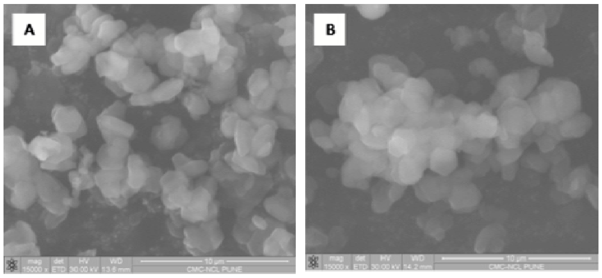

Fig. 9: SEM images of (A) calcined SBA-15 and (B) Pd(II)-DHBP@SBA-15.

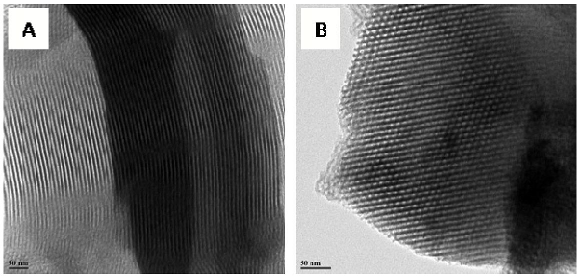

Fig. 10: TEM images of (A) calcined SBA-15 and (B) Pd(II)-DHBP@SBA-15.

–OH groups and imine N donor sites[10,11] present in 2,2'-DHBP ligand. The DR UV-Visible spectra of (a) calcined SBA-15 (b) NH_2SBA-15 and (c) Pd(II)-DHBP@SBA-15 are presented in Fig. 8. A peak at 230 nm,[25] typical for siliceous material is observed in all synthesized catalysts [Fig. 8(a-c)]. The spectra of Pd(II)-DHBP@SBA-15 [Fig. 8c] exhibits two peaks at 256 nm and 295 nm are attributed to Π →Π* transitions of the aromatic ring and the azomethine group, respectively.[26] Further, a broad peak at 367 nm is assigned to n →Π* transitions of the azomethine group. Two broad bands at 560 nm and 686 nm are assigned to N → Pd(II) & O →Pd(II) ligand to metal charge-transfer transitions (LMCT) and d-d transitions of Pd(II) species, respectively.[27] The above results also confirm the successful anchoring of Pd(II)-2,2'-dihydroxybenzophenone (DHBP) complex over SBA-15 with intact +2 oxidation state.

Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) analysis were used to attain nanometric and morphological details of the mesoporous materials. The SEM images of (A) calcined SBA-15 and (B) Pd(II)-DHBP@SBA-15 are shown in Fig. 9. The particle size of calcined SBA-15 and Pd(II)-DHBP@SBA-15 was found to be in the range of 1.10 to 1.31 μm with a hexagonal plate type structure. The morphology of Pd(II)-DHBP@SBA-15 [Fig. 9B] was retained with the parent SBA-15 [Fig. 9A] after the anchoring of Pd(II)-DHBP sites on aminofunctionalized SBA-15. The TEM images of (A) calcined SBA-15 and (B) Pd(II)-DHBP@SBA-15 are shown in Fig. 10 and its images show regular hexagonal array of uniform channels having a long-range order and well defined 1-D channels. The nanometric sized pore channels is in confirmation with SA and XRD analysis.

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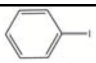
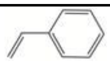
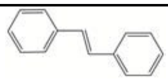
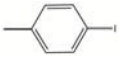
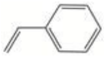
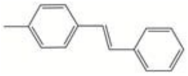
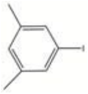
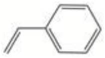
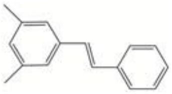
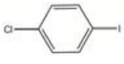
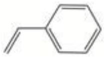
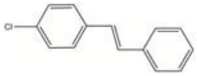
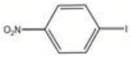
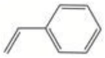
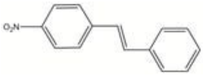
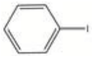
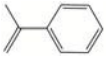
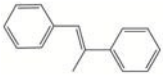
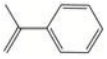
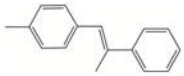
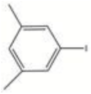
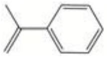
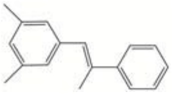
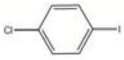
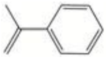
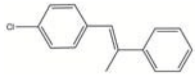
Catalytic Activity

The catalytic activity of Pd(II)-DHBP@SBA-15 complex was evaluated in arylation and hydrogenation reaction of alkenes. Arylation of alkenes (Heck reaction) in which various aryl halides couple with alkenes to give trans-stillbene derivatives, using Et$_3$N as a base and dimethylforamide (DMF) as a solvent. The reaction progress (conversion in percentage) of Pd(II)-DHBP@SBA-15 catalyst for heck reaction are shown in Table 2 (entries 1-20). To evaluate the influence of substrates, aryl halides like iodobenzene, 1-iodotoluene, 3,5-dimethyl iodobenzene, 1-iodo-4-chlorobenzene, 1-iodo-4-nitrobenzene and alkenes like styrene, α-methyl styrene, methyl acrylate, ethyl acrylate were screened, to produce coupling products **(a-t)**. The trans or *E* Isomer was formed as the dominant coupling product in all cases than Cis or *Z* isomer. As shown in Table 2, aromatic halides with electron withdrawing group (EWG) were more imprudent than that of electron donating groups (EDG). In both cases, electronic effects at para position is more predominant than meta position. Thus, the electron withdrawing group containing aryl halides (Table 2, entries 4,5) show higher and sudden conversion [95 to 100 wt.%] than electron donating groups [75 to 80 wt.%] (Table 2, entries 1-3), whereas the conversion of halides constantly decreases with increasing the number of electron donating groups. This result reveals that the presence of strong electron withdrawing group in aryl halides makes the substrate more susceptible for further oxidative-addition reactions during catalytic cycle. Likewise, EDG present in alkenes like α-methyl styrene (Table 2, entries 6-10) exhibits higher conversion towards the coupling products [87 to 100 wt.%] than a model substrate like styrene [75 to 100 wt.%] (Table 2, entries 1-5). In the case of acrylates as alkenes in Heck reactions (Table 2, entries 11-20), ethyl acrylate (Table 2, entries 16-20) shows higher conversion [90 to 100 wt.%] than methyl acrylate [90 to 95 wt.%] (Table 2, entries 11-15), due to the EDG effects. The decreasing order of reactivity of aryl halides and alkenes in Heck reactions are : 1-iodo-4-nitrobenzene > 1-iodo-4-chloro benzene > iodo benzene >1-iodotoluene > 3,5-dimethyliodo benzene and ethyl acrylate > methyl acrylate > α-methyl styrene > styrene, respectively.

Table 2: Arylation[a] of alkenes (Heck reactions)

No.	Aryl halides	Alkenes	Coupling products	Time (h)	Conv. (%)	TOF[b] (h-1)
1			 **a**	8	80	0.155
2			 **b**	10	78	0.121
3			 **c**	12	76	0.098
4			 **d**	6	95	0.245
5			 **e**	2	100	0.774
6			 **f**	8	85	0.164
7			 **g**	10	82	0.126
8			 **h**	12	78	0.101
9			 **i**	4	92	0.356

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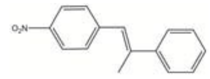
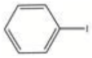
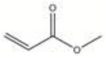
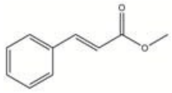
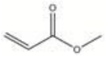
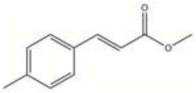
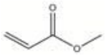
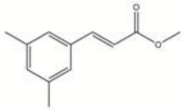
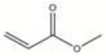
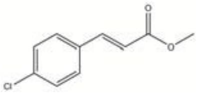
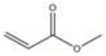
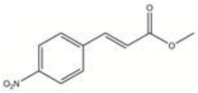
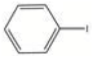
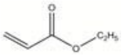
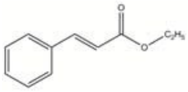
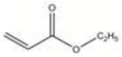
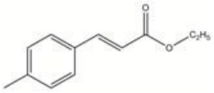
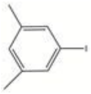
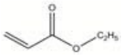
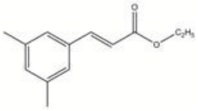
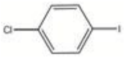
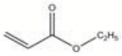
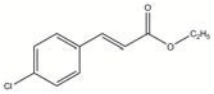
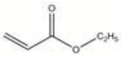
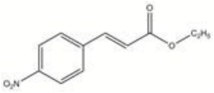
10			 j	2	100	0.774
11			 k	2	94	0.726
12			 l	4	90	0.348
13			 m	8	90	0.174
14			 n	2	95	0.735
15			 o	1	95	1.470
16			 p	2	95	0.735
17			 q	4	92	0.359
18			 r	6	90	0.232
19			 s	2	95	0.735
20			 t	1	100	1.548

[a] Reaction conditions: Pd(II)-DHBP@SBA-15: 0.015 g; aryl halide: 1 mmol; alkenes : 1.2 mmol; Et_3N: 3.5 mmol; DMF: 3.5 ml; reaction temperature: 120 °C. [b] TOF [h^{-1}] = [the number of moles of reactant converted/the number of moles of metal active sites]/time in hours.

To test the efficiency of Pd(II)-DHBP@SBA-15 complex as catalyst for hydrogenation reactions, aromatic olefins (styrene, α- methyl styrene), cyclic olefins (Cyclohexene. Cyclooctene, and 1,4-Cyclohexadiene), aliphatic olefins (I-undecene, 1-Nonene) and bicycloolefin (Bicylco[2.2.1]hepta2,5 diene) were used as substrates (Table 3, entries 1-8). All olefins showed 100 % conversion under 15 minutes to give alkanes **(i-viii)**, under ambient reaction conditions (room temperature, H_2-Pressure (5 bar) and MeOH as solvent).

In order to check the stability and reusability of Pd(II)-DHBP@SBA-15 complex, the arylation and hydrogenation reactions of alkenes with styrene as model substrate were performed under appropriate reaction conditions, which are presented in Table 4. For recyclability test, after each cycle, the catalyst was separated by filtration, washed with suitable solvent and activated for 6 h at 150 °C in an air before use in the next experiment. The synthesized catalyst showed good (fresh+ four cycle) recyclability in arylation and

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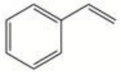
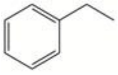
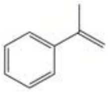
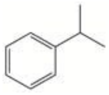
Table 3: Hydrogenation[a] reactions of alkenes

No.	alkenes	alkanes	Conv. (%)	TOF[b] (min^{-1})
1		 **i**	100	0.103
2		 **ii**	100	0.103
3		 **iii**	92	0.095
4		 **iv**	100	0.103
5		 **v**	100	0.103
6	$CH_3(CH_2)_8CH{=}CH_2$	$CH_3(CH_2)_8CH_2CH_3$ **vi**	100	0.103
7	$CH_3(CH_2)_6CH{=}CH_2$	$CH_3(CH_2)_6CH_2CH_3$ **vii**	100	0.103
8		 **viii**	100	0.103

[a] Reaction conditions: Pd(II)-DHBP@SBA-15: 0.015 g; olefins: 5 mmol; MeOH: 50 ml; H_2 Pressure: 5 bar; reaction temperature: 30 °C; reaction time: 15 min. [b] TOF [min^{-1}] = [the number of moles of reactant converted/the number of moles of metal active sites]/time in minutes.

Table 4: Recycling study of Pd(II)DHBP@SBA-15 catalyst

No. of Cycles	Arylation[a] (Styrene)		Hydrogenation[b] (Styrene)	
	Conv.	Sele.	Conv.	Sele.
Fresh	80	100	100	100
I cycle	80	100	100	100
II cycle	78	99	97	99
III cycle	73	99	91	99
IV cycle	65	98	84	99

[a] Reaction conditions: Pd(II)-DHBP@SBA-15: 0.015 g; aryl halide: 1 mmol; alkenes : 1.2 mmol; Et_3N: 3.5 mmol; DMF: 3.5 ml; reaction temperature: 120 °C; reaction time: 8 h. [b] Reaction conditions: Pd(II)-DHBP@SBA-15: 0.015 g; olefins: 5 mmol; MeOH: 50 ml; H_2 Pressure: 5 bar; temperature: 30 °C; time: 15 min

hydrogenation reactions of alkenes with retension of conversion and selectivity upto three cycles. A ~14 wt.% loss of conversion was observerd from fresh cycle in hydrogenation and Heck reactions after fourth cycle due to the 1.5 wt % leaching of palladium metal from fresh catalyst. However, all recycling studies reveals that Pd based catalyst exhibits higher stability and heterogeneous nature in each and every steps.

Conclusions

In conclusion, an efficient, simple and phosphine free Pd(II)-DHBP@SBA-15 catalyst has been synthesized by tethering of 2,2'-dihydroxybenzophenone (DHBP) ligand over aminofunctionalized SBA-15 via. post- grafting method. and Further metallation with Pd(II)Cl_2 resulted in well-ordered mesostructure with long range order. The synthesized catalysts were characterized by various characterization techniques like elemental analysis, XRD, N_2 sorption analyses, TG, DTA, FT-IR, solid state ^{13}C and ^{29}Si NMR spectra, XPS, UV-Visible, SEM, EDAX and TEM. All characterization techniques proved that mesoporous SBA-15 and synthesized catalysts retained its structural integrity, textural properties, organic moieties, oxidation state, morphology and topographic characteristics after heterogenization. The catalytic activity of Pd(II)-DHBP@SBA-15 was screened in arylation and hydrogenation reactions of alkenes, and the results show that Pd(II)-DHBP@SBA-15 exhibits high conversion and selectivity towards arylation and hydrogenation reactions of alkenes in combination with high stability. The electronic (EWG & EDG effects) and steric effects (bulkier group) of groups on the substrates are also probed and the trend follow those reported in literature. In addition, aliphatic olefins or less hindered olefins like acrylates gave better conversion and selectivity than aromatic olefins like substituted styrene. Due to these reasons, in Heck reaction, 4-nitro-1-iodobenzene showed higher reactivity with ethyl acrylate to give the coupling products with 100 % conversion and selectivity within 1 h. Moreover, in hydrogenation reactions, all olefins, except conjugated olefins, showed 100 % conversion under 15 mintues to give alkanes, under mild conditions. The recyclability test was carried out to confirm the stability and heterogeneousous nature of catalyst and the results concluded that that Pd(II)-DHBP@SBA-15 is reusable without much loss of activity for several cycles.

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An efficient, phosphine and co-catalyst free Pd(II)-DHBP@SBA-15 catalyst for arylation and hydrogenation reactions of alkenes was synthesized and characterized.