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Palladium(II) supported on polycarbosilane: Application as reusable catalyst for Heck reaction

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ABSTRACT

Heck reaction catalyzed by palladium(II) attached polycarbosilane is reported. Polycarbosilane (PCS), which is an organic-inorganic hybrid polymer containing both Si and C in its back bone structure, was synthesized by the polycondensation of trichloromethylsilane and trimethoxyvinylsilane in the presence of sodium metal. Palladium acetate was attached to the polycarbosilane (Pd-PCS) and its catalytic activity was investigated. Heck reaction in which C–C coupling between aryl halides or vinyl halides and activated alkenes in the presence of a base has been selected for the study. Palladium ions supported on PCS have been used as a catalyst for the first time and it efficiently catalyzed Heck reaction and an yield of 75–90% was obtained with different substrates. For comparison, catalytic activities of Pd ions supported on SBA-15, activated charcoal and amorphous silica were also investigated. Results indicate the superior activity of Pd-PCS.

1. Introduction

Polycarbosilane (PCS) has considerable technological importance due to its high thermal, chemical and oxidative stability. It is not hard to envision a variety of potential applications that are opening up for these polymers in areas such as nanotechnology [1], surface science, catalysis [2–6], liquid crystals [7–9], new ceramic materials [10–14], organic-inorganic hybrids etc. PCS, which contains both Si and C in their back bone structure, have been of particular importance as precursor to SiC [15–21]. PCS can be prepared in one step from simple silane monomers or mixtures containing vinyl, halo or halomethyl moieties in the presence of an active metal. Several investigators have explored the use of alkali metals for the reductive coupling of silanes and vinyl silanes [11–14,16,18–21]. The participation of vinyl groups produces partial branching. The Wurtz type coupling reaction, which employs alkali metals, can be used for the preparation of PCS. It generally leads to extensive crosslinking and appreciable Si—Si and C—C bonding in addition to SiC bonding [15–17]. A reasonable ceramic yield is obtained after sufficient crosslinking which increases the softening temperature and decreases the solubility. The highly crosslinked nature of the PCS provides scope for high surface area for the polymer [4,5]. High surface area is one of the main criteria for materials which are used as solid supports in heterogeneous catalysis.

Homogeneous catalytic processes often exhibit high activity and selectivity, in most cases, but the catalyst-product separation is generally nontrivial. In addition, the metal catalysts and ligands can be very expensive. These limit the practical application of many outstanding catalytic systems. Immobilization of analogues of homogeneous catalysts on a solid support is one of the promising ways to prepare well-defined catalytic systems, a task of great economic and environmental importance [22–24]. Palladium catalysts deposited over different types of solid supports such as silica matrices, charcoal etc have been reported [25–28]. However, activated charcoal and non-functionalized polymers have drawbacks such as relatively low stability or lack of active functional groups for binding Pd ions and hence the inherent restrictions for reuse [28]. Since C and SiO_2 have only a small residual charge, their affinity for metal ions will be weak. Silica is a favorable solid support, but if silica is used directly, the main problem of these catalytic systems seems to be the metal leaching from the support during the reaction even though they adsorb back to the support after the completion of the reaction [27]. Polymer supported transition metal ions have significant role as catalysts in various organic reactions [4,5,29,30]. The metal ions are attached to the polymer support through a chemical bond. This reduces the possibility of leaching of metal ions from the solid support. Considering Pd ions as a homogeneous catalyst, they easily lose catalytic activity by forming Pd clusters and also they are highly expensive. A heterogeneous catalyst is desirable in this

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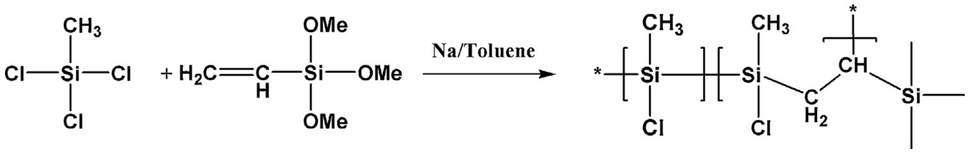


Scheme 1. Synthesis of polycarbosilane.

case, especially for recycling, though it is not always as reactive as compared to homogeneous catalysts.

Palladium catalysis has achieved the status of an indispensable tool for both common and state-of-the art organic synthesis. Among basic types of palladium catalysed transformations, the Heck reaction and related chemistry occupies a special space. Heck reaction is the catalytic arylation and alkenylation of olefins [31–35]. The reaction presents one of the simplest ways to obtain variously substituted olefins, dienes, and other unsaturated compounds. Aryl, benzyl, and styryl halides react with olefinic compounds in the presence of hindered amines and a catalytic amount of palladium ions to form vinyl derivatives in which the aryl, benzyl, or styryl group has replaced a vinyl hydrogen of the original olefin. To satisfy both recyclability and reactivity, immobilization of a reactive homogeneous catalyst was devised by binding the Pd catalyst on a polymer. Polycarbosilane is an active support for the heterogeneous catalysis. The PCS shows high thermal stability and have crosslinked structure. By altering the monomers and reaction time, it is possible to get sufficient crosslinking and active sites in the polymer. The metal salts react with the active sites of the PCS and stable bonds are formed between them, thus developing an efficient heterogeneous catalyst. $Pd(OAc)_2$ was chosen as Pd source for the current study. For comparison, catalytic activities of Pd ions supported on SBA-15 (Pd-SBA), activated charcoal (Pd-C) and amorphous silica (Pd-SiO_2) were also investigated. Pd-PCS show high stability, negligible metal leaching and can be reused with same activity. This indicates the superiority of PCS with other supports under consideration.

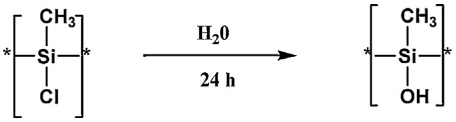
2. Experimental

2.1. Materials

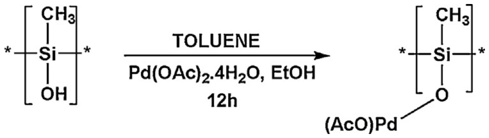
Monomers, trichloromethylsilane and trimethoxyvinylsilane, palladium acetate, SBA-15 and palladium(II) attached charcoal were purchased from Sigma–Aldrich, USA. DMF, triethyl amine, sodium, amorphous silica and sodium sulphate were purchased from Loba Chemie Pvt. Ltd., India. Chloroform, dichloromethane, diethyl ether, ethanol, methanol, toluene and all the substrates for catalytic activity studies were purchased from Spectrochem Pvt., Ltd., India; and all the solvents were purified according to standard procedures [36].

2.2. Characterization

FT-IR spectra were recorded on JASCO model 4100 FT-IR spectrometer as KBr pellets. ^{29}Si-CP-MAS NMR and ^{13}C CP-MAS-NMR spectra were obtained from NMR Research Center, IISc., Bangalore and National Chemical Laboratory, Pune. Thermogravimetric analysis was done on PerkinElmer Diamond model Pyris 6 TG/DTA system using Platinum as standard. Samples were heated under nitrogen atmosphere from 50 °C-1000 °C at a rate of 20 °C/min. The X- Ray Diffraction analysis was carried out using Rigaku (D-MAX Cu-Kα) X-ray Photometer. The sample was scanned over the range of 20–90° angles with an increment of 0.05° angle and with the rotation speed of 5°/min. (SAIF-CUSAT). Surface Area & porosity were measured using Micromeritics TriStar 3000 V6.07 A Surface area analyzer. The metal ion concentration was estimated using Thermo Electron Corporation Atomic Absorption Spectrometer. ^{1}H NMR spectra were recorded on Bruker 400 MHz instrument with TMS as the internal standard in $CDCl_3$ (SAIF-CUSAT). In catalytic activity study, all the reactions were analyzed, by HPLC on Shimadzu CLASS VP Ver 6.1. Column: Phenomenex Luna 5u C18 (2) 100 Å, for yield and purity of the products. Solvent ratio (CH_3OH:H_2O) was 75:25 with a run time of 30 min. The flow rate, detector wavelength and the temperature were 1 mL/min, 254 nm and 28 °C, respectively.



Scheme 2. Conversion of chloride groups of PCS to hydroxyl groups.



Scheme 3. Incorporation of palladium ion to PCS.

2.3. Synthesis of PCS

In a 250-mL round-bottom flask, sodium metal (2.5 g, 108.75 mmol) was refluxed in anhydrous toluene (50 mL) and stirred vigorously to make dispersion. A mixture of trichloromethylsilane (6.4 mL, 54.38 mmol) and trimethoxyvinylsilane (8.3 mL, 54.38 mmol) was added drop wise carefully (Scheme 1). The reaction was highly exothermic. After the addition of monomers, the reaction mixture was refluxed for 12 h. The whole process was carried out in a fume hood and under Nitrogen atmosphere. The reaction mixture was cooled and the suspension obtained was filtered and washed initially with methanol, then with water in a Soxhlet extractor for 24 h, and dried under vacuum. Yield was 47%. Chlorine estimation was done by the modified Volhard's method [4,6,37].

2.4. Preparation of hydroxyl substituted PCS

PCS was treated with water to substitute chloro substituent with hydroxyl groups. The reaction was conducted in a round bottom flask; the polymer was refluxed in water for 24 h (Scheme 2). It was cooled and the precipitate obtained was filtered and dried under vacuum.

2.5. Preparation of polycarbosilane supported palladium ion (Pd-PCS)

1 g of PCS was stirred in 15 mL of dry toluene for 12 h to swell. Ethanolic solution of palladium acetate (1.35 g, 6 mmol) was added drop wise to the swollen PCS and was stirred for 12 h under reflux condition (Scheme 3). The reaction mixture was cooled, filtered,

and washed with methanol in a Soxhlet extractor and dried under vacuum.

2.6. Catalytic activity study

Heck reaction was considered as the model reaction to study the catalytic activity of Pd-PCS. The optimum quantity of the catalyst was found out first and the catalytic activity was generalized by conducting the reaction with diverse sets of substrates. To optimize the concentration of catalyst, the reaction between 1-iodo-4-nitrobenzene and acrylonitrile was conducted in the presence of Pd-PCS by varying the concentration as 2, 3, 5 and 10 mol%. Yield of the reaction was analyzed in each case. General procedure for Heck reaction: To a round bottom flask containing 3 mol% of Pd-PCS, mixture of organic halide (1 equiv.), olefinic compound (1 equiv.) and triethyl amine (1 equiv.) were added. DMF was used as the solvent. A water cooled condenser was placed on the flask and stirred for about 8 h at 100 °C. The reaction mixture was cooled, filtered and washed initially with dichloromethane and then with water. The filtrate was extracted with diethyl ether. The ether layer was collected and dried over anhydrous sodium sulphate. It was filtered and solvents were removed in a rotary vacuum evaporator. The residue was recrystallized from dichloromethane.

For the comparative study of catalytic activity, Heck reaction in the presence of Pd-SBA, Pd-C and Pd-SiO$_2$ were also conducted. [Pd-SBA and Pd-SiO$_2$ were prepared by stirring an ethanolic solution of palladium acetate (1.35 g of palladium acetate in 15 mL of ethanol) with 1 g of SBA-15/SiO$_2$ for 12 h under reflux condition. The reaction mixture was cooled, filtered, and washed with methanol in a Soxhlet extractor and dried under vacuum. The supports were heated to 300 °C prior to use]. The reaction was conducted between 1-iodo-4-nitrobenzene and acrylonitrile in the presence of 3 mol% of catalyst.

2.6.1. Recycling of catalysts

Recycling of the catalysts were performed as follows: The Heck reaction between 1-iodo-4-nitrobenzene and acrylonitrile was carried out by taking equimolar amounts of substrates and trimethyl amine in a round bottom flask containing 3 mol% of catalyst. DMF was used as the solvent and the reaction was carried out for about 8 h at 100 °C. The reaction mixture was cooled and catalyst was removed by simple filtration. It was washed thoroughly with methanol, chloroform and acetone and dried under vacuum for 24 h. The recovered catalyst was used again for carrying out the reaction in each cycle.

3. Results and discussion

3.1. Preparation of PCS

The preparation of PCS by the polycondensation of chlorosilane and vinyl silane in the presence of a metallic reducing agent has been demonstrated in Scheme 1. Trichloromethylsilane and trimethoxyvinylsilane were used as monomers. The mixture of monomers was refluxed with sodium in toluene for 12 h; polymer was formed by Wurtz-type coupling reaction which led to the formation of hyper branched PCS back bone with appreciable Si—Si and C—C bonding, in addition to Si—C bonding [12–14,18,38,39].

The quantitative estimation of chlorine in PCS was done by the modified Volhard's method. The result showed that 4.10 m.equiv./g of chlorine was present in the polycarbosilane.

The FT-IR spectrum of the polymer showed the corresponding peaks of PCS [20]. Peaks at 1453, 1270, 1082, 783 cm^{-1} could be clearly seen in the spectrum which corresponded to the CHSiCH$_3$ and SiC. The spectrum showed a peak at 2929 cm^{-1} which was corresponding to the CH stretching, 1635, 1453 cm^{-1} due to SiCH$_3$ stretching, 1270 cm^{-1} corresponding to SiCH$_3$ deformation,1082 cm^{-1} due to CH$_2$ wagging in SiCH$_2$Si bond and 783 cm^{-1} due to SiCH$_3$ wagging. 1032 cm^{-1} seen as superimposed on 1082 cm^{-1} was assigned to SiO bonds. The peaks assigned to SiOSi bonds (around 1040 cm^{-1}) was observed since this peak intensified with prolonged air exposure, the side chains of the polymer might have got oxidized during the handling and recording processes.

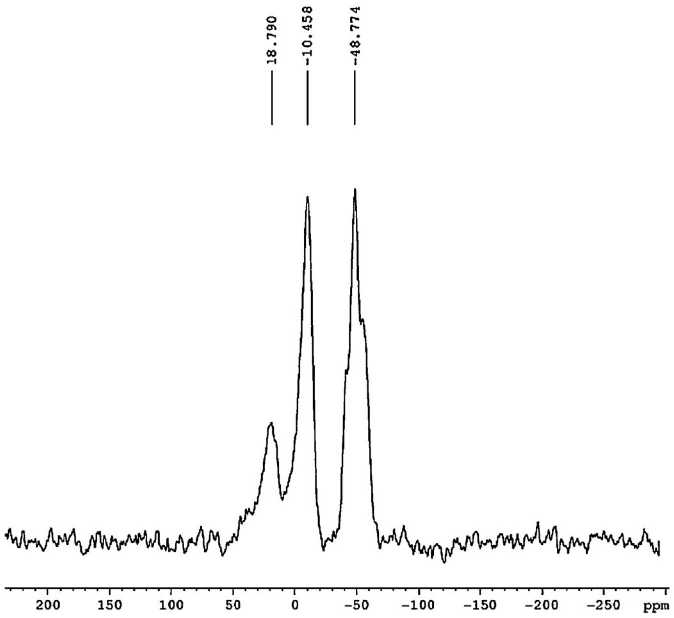


Fig. 1. ^{29}Si CP-MAS NMR spectrum of PCS.

^{29}Si CP-MAS NMR spectrum of PCS is shown in Fig. 1. Spectrum gives a clear idea about the structure of the polymer. Peaks were mainly distributed in two regions. Peak around −10.45 ppm corresponds to CH$_3$SiCl(CH$_2$)$_2$ linkage and −48.77 ppm peak is of SiSi linkage; formed by the head to head polymerization of the monomers. A small peak at 18.79 ppm corresponds to Si—O linkage which might be formed by the oxidation of the polymer side chains.

Fig. 2 shows the ^{13}C CP-MAS NMR spectrum of PCS. It exhibits two major broad peaks at 6.03 and 14.45 ppm, which are mainly assigned to the signal of SiSiCH$_3$ units and CH$_2$-CH$_2$ respectively. The absence of signal around 60 ppm indicates the absence of unreacted alkoxy group in the prepared polymer.

In the TG curve (Fig. 3), 3% weight loss below 300 °C is attributed to the vaporization of low molecular weight oligomers and physically adsorbed water from the polymer surface. From 300–800 °C the main weight loss indicates that the polymer undergoes Kumada rearrangement and releases gaseous products such as methane and hydrogen during the conversion of the Si—Si bond to Si—C bond. No obvious weight loss was observed in the range of 800–1000 °C. The total weight loss of the polymer at 1000 °C was found to be only 14%. High temperature stability is attributed to substantial crosslinking in PCS [16].

The XRD pattern of the PCS (Fig. 4) clearly reveals its amorphous nature; which can be explained because of it's highly crosslinked structure.

From the spectral data, it is clear that the PCS has Si—Si, Si—C and C—C linkage and also all the methoxy groups have been reacted to form the polymer. Halide estimation implies the presence of chlorine in polycarbosilane. The polymerization was conducted in an oxygen free atmosphere. Hence the SiO linkage might be formed by the oxidation of the polymer side chains.

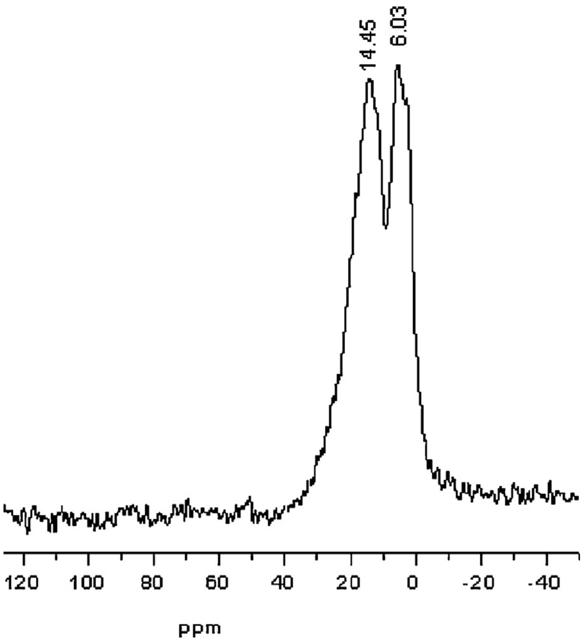


Fig. 2. ^{13}C CP-MAS NMR spectrum of polycarbosilane.

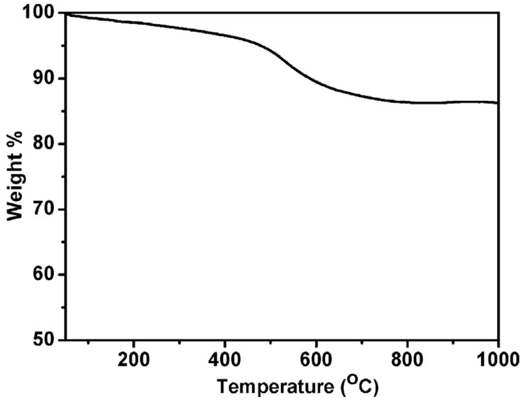


Fig. 3. TG curve of polycarbosilane.

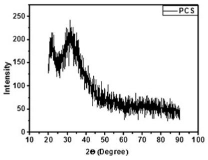


Fig. 4. X-ray diffraction pattern of polycarbosilane.

4. Preparation of Pd-PCS

PCS was refluxed in water, to substitute the chloro groups with hydroxyl groups (Scheme 2). The hydroxyl group substitution was confirmed from the infrared spectrum, which showed a peak around 3448 cm^{-1}.

The hydroxyl substituted PCS was allowed to swell in toluene. Palladium acetate was added to it as an ethanolic solution and stirred at reflux condition (Scheme 3). Pd-PCS was characterized by FT-IR, ^{29}Si-CP-MAS NMR, ^{13}C CP-MAS NMR spectroscopic techniques, TG-DTA, AAS and surface area analysis.

The FT-IR spectrum of the Pd-PCS showed the peak corresponding to SiOPd at 980 cm^{-1}.

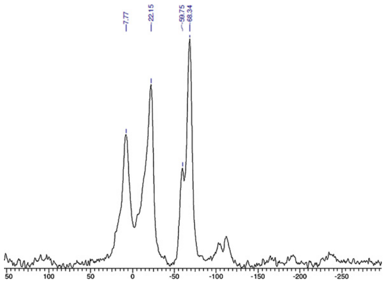


Fig. 5. ^{29}Si CP-MAS NMR spectrum of Pd-PCS.

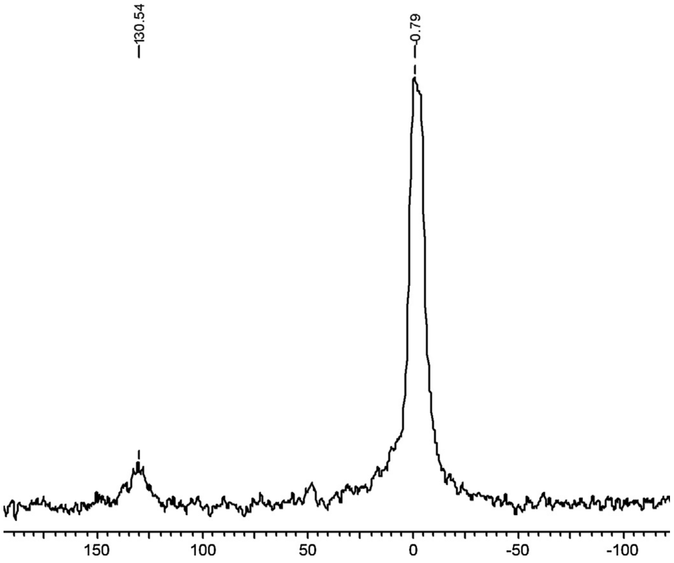


Fig. 6. ^{13}C CP-MAS NMR spectrum of Pd-PCS.

The metal content of the polymer was determined using AAS technique. The AAS result showed that 4.28 m.equiv/g of palladium ion was present on the polycarbosilane.

^{29}Si CP-MAS NMR spectrum of Pd-PCS is shown in Fig. 5. New peaks in the region around −102.64 and −111.97 ppm correspond to the PdOSi linkage. It is seen that there is a total up field shift of the polycarbosilane peaks. Peak around −10.45 ppm has been shifted to −22.15 ppm and −48.77 ppm to −68.34 ppm and small peak around 18.79 ppm was shifted to 7.77 ppm. This trend is explained due to the presence of palladium ion attached to the polycarbosilane.

^{13}C CP-MAS NMR spectrum of Pd-PCS is shown in Fig. 6. Signals around 130 ppm and −0.79 ppm are observed. Peak around −0.79 ppm is due to the polycarbosilane and the former one *ie*, 130 ppm corresponds to the peaks of acetate moiety.

From the above data it could be confirmed that the palladium ion was attached to the PCS through Si—O—Pd linkage and the acetate moiety was also attached to the metal.

The thermogravimetric analysis of Pd-PCS shows very small weight loss, which might be because of the evaporation of adsorbed water molecule and low molecular weight fractions of the polycarbosilane.

Surface area of the prepared polycarbosilane and Pd-PCS were determined by BET surface area analyzer. Results are shown in Table 1. The surface area of both the PCS and Pd-PCS were found to be high. The high surface area of PCS can be explained by its mesoporous nature. The high surface area is a supportive aspect for the application of PCS in catalysis.

Table 1
Results of BET surface area analysis.

Sample	Surface area (m2/g)	
	BET	Langmuir
PCS	679	1171
Pd-PCS	311	480

Table 2
Optimization of amount of the catalyst*

Entry	Mol (%) of the catalyst	Yield (%)
1	2	83
2	3	92
3	5	93
4	10	98

* Catalyst- Pd-PCS and time 8 h.

Table 3
Heck reaction with different substrates*

Entry	Organic halide	Olefinic compound	Yield (%)
1	4- Iodotoluene	Acrylonitrile	83
2	1-Iodo-4-nitrobenzene	Acrylonitrile	92
3	4- Iodotoluene	Styrene	75
4	1-Iodo-4-nitrobenzene	Styrene	79
5	4- Iodotoluene	Methyl acrylate	77
6	1-Iodo-4-nitrobenzene	Methyl acrylate	80
7	4- Iodotoluene	Methyl methacrylate	79
8	1-Iodo-4-nitrobenzene	Methyl methacrylate	83
9	4-Iodobenzoic acid	Acrylonitrile	86
10	4-Iodobenzoic acid	Methylmethacrylate	90

* Reaction condition- equimolar conc. of aryl halide and olefinic compound in the presence of 3 mol% of Pd-PCS at 100 °c and time 8 h.

Table 4
Metal content on solid supports.

Catalyst	Pd(II) content (m. equiv./g)
Pd-PCS	4.28
Pd-SBA	0.88
Pd-SiO2	0.57
Pd-C	0.94

Table 5
Recycling of catalysts* .

Catalyst	Yield (%)		
	1st cycle	2nd cycle	3rd cycle
Pd-PCS	92	90	89
Pd-SBA	90	50	26
Pd-SiO$_2$	93	40	23
Pd-C	92	40	24

* Catalyst- 3% Pd-PCS, temperature 100 °C and time 8 h.

4.1. Catalytic activity study

Palladium ions attached to the polymer were considered as the catalytic sites and polycarbosilane as solid support. The amount of catalyst was estimated in terms of the palladium ions with respect to the substrates. The catalytic activity study was done by conducting the Heck reaction in the presence of Pd-PCS. To examine the effect of catalyst concentration, the reaction of 1-iodo-4-nitrobenzene and acrylonitrile in the presence of Pd-PCS was conducted. The study proceeded by conducting the reaction using different amounts of Pd-PCS. The results of the study are given in Table 2.

It was observed that, as the metal concentration was increased, the rate of the reaction was also increased. From the results obtained and by considering the expense of palladium salts, the optimum concentration of catalyst was selected as 3 mol% with respect to the aryl halide; and DMF as the solvent, 100 °C as reaction temperature and time period of the reaction as 8 h.

The catalytic activity of Pd-PCS was generalized by conducting the Heck reaction with diverse sets of substrates, which are listed in Table 3. The products were known compounds and identified by comparing the spectral data (FT-IR, ^{1}H NMR spectra and mass spectra by LCMS) and melting points with those reported. All the reactions were analyzed by HPLC for yield and purity of the products. One of the benefits of the Heck Reaction is its outstanding trans selectivity. The spectral data of selected entries are listed below.

Entry 1: (E)-3-p-tolylacrylonitrile, $C_{10}H_9N$

LCMS ES$^+$ (M$^+$-1) *m*/*z*: 142; FT-IR (KBr, cm^{-1}): 3037, 2932, 2258, 1587, 1320, and 977; H^1 NMR (400 MHz, CDCl$_3$) δ: 7.39, 7.35 (d, 1H, *J* = 16 Hz), 7.49,7.33 (d, 1H), 7.22, 7.20 (d, 1H), 5.84, 5.80 (d, 1H, *J* = 16 Hz), 2.38 (s, 3H); M. p.: 48 °C.

Entry 5: (*E*)-Methyl 3-*p*-tolylacrylate, $C_{11}H_{12}O_2$

LCMS ES$^+$ (M$^+$+1) *m*/*z*: 177; FT-IR (KBr, cm^{-1}): 3055, 2930, 1747, 1346 and 987; H^1 NMR (400 MHz, CDCl$_3$) δ: 7.69, 7.65 (d, 1H, *J* = 16 Hz), 7.43 (d, 2H), 7.20 (d, 2H), 6.41, 6.37 (d, 2H, *J* = 16 Hz), 3,80 (s, 3H), 2.37 (s, 3H); Pale yellow oil.

Entry 7: (*E*)-Methyl 2-methyl-3-*p*-tolylacrylate, $C_{12}H_{14}O_2$

LCMS ES$^+$ (M$^+$+1) *m*/*z*: 191; FT-IR (KBr, cm^{-1}): 3087, 2932, 1747, 1320, and 967; H^1 NMR (400 MHz, CDCl$_3$) δ: 8.15 (m, 1H), 7.89 (d,1H), 7.76 (m, 1H), 7.74 (d,1H), 7.25, 7.21 (d, 1H, *J* = 16 Hz), 3.54 (m, 3H), 2.51 (s, 1H) 1.94 (m, 3H). Oily in nature.

It is clear that Pd-PCS efficiently catalyzed the reaction, almost 75–90% yields were obtained for all substrates under consideration. The product analysis gives an idea about the trans-selectivity of catalyst.

In order to compare the catalytic activity of Pd-PCS, Heck reaction in the presence of Pd-SBA, Pd-C and Pd-SiO$_2$ were also conducted. The metal ion content of the Pd-C, Pd-SBA and Pd-SiO$_2$ were determined using AAS technique. The results are listed in Table 4. It is evident from the result that the metal ion attachments were low compared to Pd-PCS and it might be because; palladium ions were attached to the solid supports only by adsorption.

4.1.1. Comparative study of catalytic activity

For the comparative study of catalytic activity, Heck reaction was conducted between 1-iodo-4-nitrobenzene and acrylonitrile in presence of 3 mol% of Pd-SBA, Pd-SiO$_2$ and Pd-C.

Experiments were also carried out to examine the recyclability of catalysts, by conducting the Heck reaction of 1-iodo-4-nitrobenzene and acrylonitrile under optimized reaction conditions. The results are entered in Table 5. The results indicate that catalysts show almost similar activity in the first cycle. The reaction proceeded smoothly for the three cycles when Pd-PCS was used as the catalyst. But in the case of other catalysts, as the number of cycles increases the activity reduces. It may be because of the leaching out of metal ions from the support in each cycle. As a result, the product yield gradually decreased in successive cycles.

The AAS analysis of the recycled catalysts shows that the leaching of Pd(II) ion from the PCS support was insignificant. But Pd-SBA, Pd-SiO$_2$ and Pd-C show significant leaching. The dramatic decrease in the Pd dispersion during the reaction leads to a significant decrease in catalytic activity of the catalysts in further cycles.

Pd-PCS shows high thermal stability, which may be necessary for Heck reaction. The PCS is an active support so that when Pd(OAc)$_2$ was added a stable chemical bond was formed. The unfavorable leaching was minimized because of this linkage.

5. Conclusion

Highly crosslinked PCS was successfully synthesized and characterized. The study showed the application of PCS in the area of heterogeneous catalysis. The cross linked nature increases the surface area of the polycarbosilane, which is one of the main advantages in catalysis. Heck reaction was considered for the catalytic activity study of Pd-PCS. Reaction with a diverse set of substrates was examined and good to excellent yield was obtained. Catalysts such as Pd ions supported on SBA-15, activated charcoal and amorphous silica were also used in order to compare the catalytic activity of Pd-PCS. Results indicate the superior activity of Pd-PCS.

In summary, the article demonstrates an environmentally benign, economically friendly and sustainable Heck reaction, employing $Pd(OAc)_2$ supported on PCS. The catalyst was air-stable and thermally stable to allow easy use and storage without any precautions and shows high recyclability, which would enable wide application in various Pd-catalyzed reactions.

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