Volume 1 | Number 1 | Jan 2013 | Pages 1–100

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Graphical Abstract

Palladium nanoparticles supported on triazine functionalised mesoporous covalent organic polymers as efficient catalysts for Mizoroki-Heck cross coupling reaction

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A palladium nanoparticles supported on nitrogen rich mesoporous covalent organic polymers material exhibiting excellent catalytic activity towards Mizoroki-Heck cross coupling reaction.
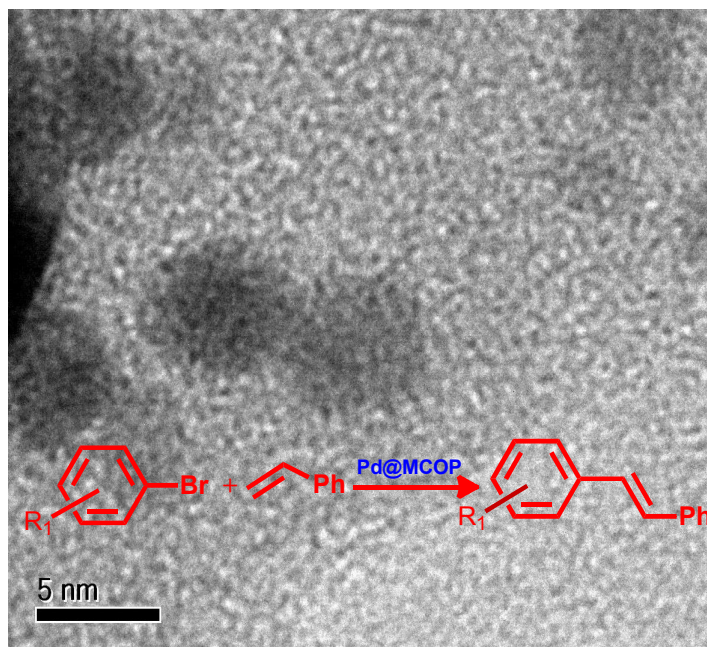
Palladium nanoparticles supported on triazine functionalised mesoporous covalent organic polymers as efficient catalysts for Mizoroki-Heck cross coupling reaction

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Abstract

A novel class of mesoporous covalent organic polymers (MCOPs) were synthesised involving nucleophilic substitution of cyanuric chloride with 4,4'-dihydroxybiphenyl. These MCOPs were fully characterized using powder X-ray diffraction (PXRD), Fourier Transform Infrared (FT-IR), ^{13}C-solid state NMR, Field Emission Scanning Electron Microscopy (FE-SEM) and Thermogravimetric analyses (TGA). This nitrogen rich material acts as a good support for palladium nanoparticles (Pd NPs) exhibiting excellent catalytic activity towards Mizoroki-Heck cross coupling between aryl bromides and alkenes. Hot filtration tests demonstrate that the presence of the triazine rings on the polymers is beneficial for enhancing the stability of Pd NPs. The polymer is also cheap, easy to syntheses and can be recycled upto five times with only minor loss in its activity.

Keywords: Mesoporous Covalent Organic Polymer, Palladium nanoparticles, Mizoroki-Heck cross coupling, Triazine based polymer, Heterogeneous catalyst.

Introduction

Covalent organic polymers (COPs) are a new class of emerging light weight micro/meso porous materials ingeniously formed by strong covalent linkages between C, Si, B, N and O.[1] These materials contain well-defined, predictable two dimensional (2D) or three dimensional (3D) ordered porous architectures,[2] similar to that of metal-organic frameworks (MOFs).[3] These materials have advantages, such as light weight, low density, cheap and easy synthesis, tenability, high stability to thermal treatment with water and most of the organic solvents, high thermal stability and permanent porosity.[1] Based on these advantages, the COPs materials have found various applications of technical relevance in separation, gas storage, gas purification, drug delivery, sensor, semiconductive and photoconductive devices, charge carrier and catalysis.[4] Consequently the inclusion of multifaceted functionality into porous networks is one of the frontline areas of research, which could lead to synthesis of new materials with diverse applications. For example, incorporation of an active functionality, namely, nitrogen on the surfaces of the supported materials may be beneficial to enhance the catalytic performance as well as the stability of the supported materials.[5] Recently, we have reported triazine based mesoporous covalent imine polymers as novel solid supports for copper mediated Chan-Lam cross coupling of *N*-arylation reaction.[5b] Some of the porous organic frameworks (POFs) and nanoparticles supported POFs materials have been used as catalysts in organic reactions.[6] As some of the porous materials based supports used to include the nanoparticles are unstable in aqueous and most of the organic solvents, tedious synthetic protocols are needed for their synthesis and as well as usage of these catalysts.[7] In order to overcome these issues, we believe that the synthesis of new porous materials having strong interaction between support and loaded metals with high stability is desirable.

2

Palladium-catalyzed Heck reaction of aryl halides with alkenes is one of the most important and versatile tool for C-C bond forming processes in synthetic and medicinal chemistry in the search of new derivatives with wide ranging therapeutic potentials.[8,9] Over the decades, various homogeneous catalytic systems have been developed for this transformation, which always exhibit better activity and selectivity.[10] Although many organometallic compounds with special ligands have been used as catalysts in this reaction, most of them suffer from drawbacks such as high ligand sensitivity towards air and moisture, tedious multistep synthesis and work-up, high cost of the ligands and use of various additives and harmful organic solvents. Furthermore, potential application of homogeneous catalytic systems in industry is limited due to the difficulties in separation, recovery and reusability and metal leaching of these expensive catalysts.[11] Thus the current challenge for palladium catalyzed coupling reactions is development of high performance catalysts in sustainable and environmentally benign reaction conditions.[12] Thus, the search for heterogeneous technologies that are greener, safer, environmentally friendly and reusability is a research priority, particular for the chemical and pharmaceutical industries. Recently, our group reported the palladium aminocyclodextrin complex as an efficient catalyst for Heck cross coupling.[13] However, Pd NPs, an important kind of heterogeneous catalysts, are prone to aggregate and lose their catalytic activity without the use of a stabilizer.[14] Therefore, they need to be supported on solid materials (such as carbon frameworks, silica, silica carbon composites and metal-organic frameworks) to be useful as catalyst for Heck reactions.[15] In addition, in many cases, the catalytic active sites may be lost due to the leaching of palladium in supported systems which makes the catalyst difficult to recover and reuse.[12] Therefore, the need for a suitable supports for Pd NPs catalysts is an important goal in heterogeneous catalysis. Recently, Zhang *et al.* have been reported mesoporous silica supported palladium nanoparticles as efficient and reusable catalyst for Ullmann reaction in water-medium.[16] In

this context, nitrogen rich triazine based POFs may incorporate a large number of metal binding sites. Herein, we first report a novel strategy for the synthesis of new mesoporous covalent organic polymers supported Pd NPs for use in Heck reaction under eco-friendly conditions. The porous organic polymers materials have been synthesised through a simple nucleophilic substitution of relatively cheap, industrially important and readily accessible chemicals.

Result and Discussion

The triazine based mesoporous covalent organic polymer (MCOP) was synthesised by the nucleophilic substitution between cyanuric chloride and 4,4'-dihydroxybiphenyl as depicted in scheme 1. The synthesised material was thoroughly characterized by fourier transform infrared (FT-IR), ^{13}C cross polarization-magic angle spinning (CP-MAS) NMR spectroscopy, field emission-scanning electron microscopy (FE-SEM), powder XRD, thermogravimetric analysis (TGA) and nitrogen gas adsorption studies. The synthesised MCOP material is insoluble in water and common organic solvents such as DMF, THF, DMSO, acetone, *etc*.
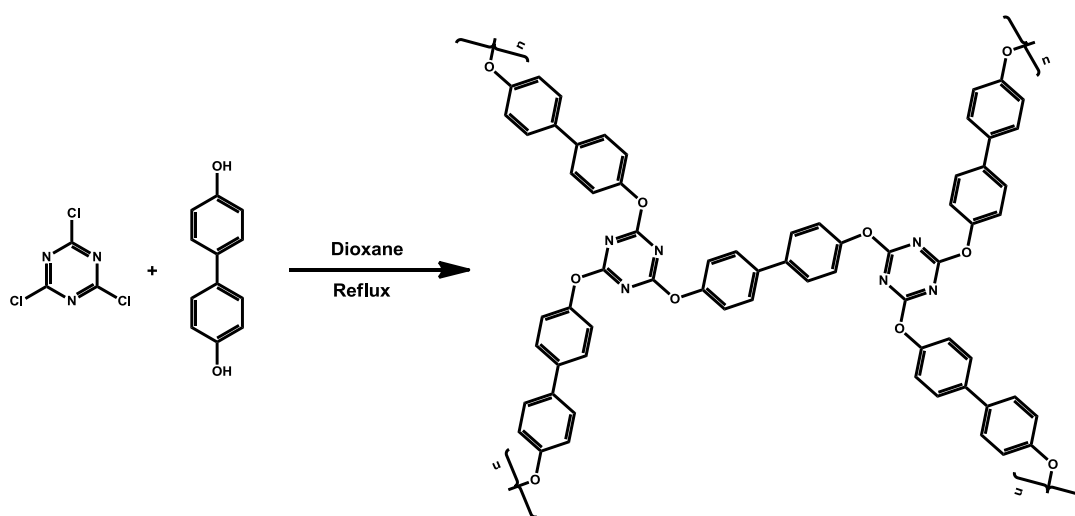
Scheme 1. Schematic representation of mesoporous covalent organic polymer (MCOP)

4

In FT-IR spectra of MCOP (Figure 1), the bands at 1249 cm^{-1} and 1562 cm^{-1}, indicate the presence of C-O-C bond and triazine units. The C-Cl stretching at 851 cm^{-1} has completely diminished, suggesting the conversion of starting cyanuric chloride.
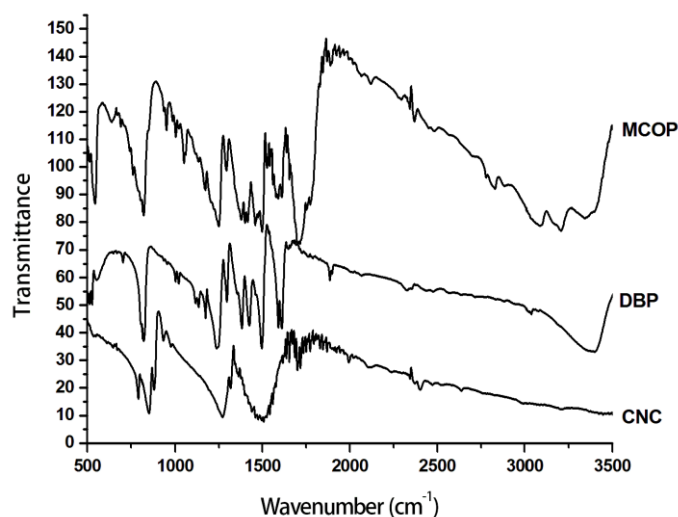

Fig. 1. FT-IR spectra of cyanuric chloride (CNC), 4,4'-dihydroxybiphenyl (DBP) and MCOP

The ^{13}C-cross-polarization magic angle spinning (CP-MAS) NMR spectral data (Figure 2) clearly confirmed the chemical structure of the synthesised MCOP material. The solid state NMR shows five peaks at 122.2, 127.1, 137.4, 151.4, 173.5 ppm. The peak at 173.5 ppm corresponds to the triazine carbon. The peak at 151.4 ppm corresponds to the carbon atom of the oxygen attached biphenyl. The signals at 122.2, 127.1 and 137.4 ppm can be assigned to the carbon atoms of the phenyl rings. Thus, the NMR data clearly confirm that the polymer was formed from cyanuric chloride and 4,4'-dihydroxybiphenyl.
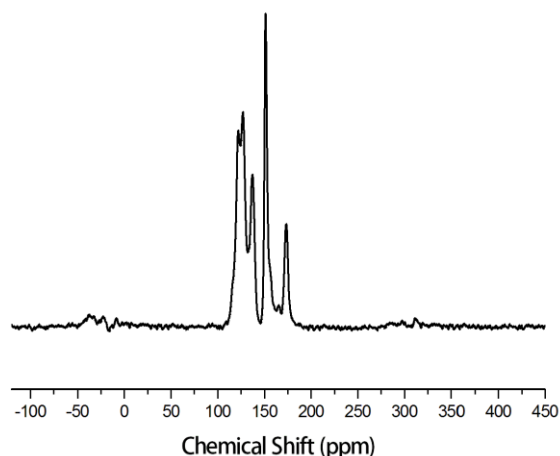
Fig. 2. ^{13}C CP-MAS NMR spectrum of MCOP

Field Emission Scanning Electron Microscopy (FE-SEM) and High Resolution-Transmission Electron Microscopy (HR-TEM) images describe the morphology and porosity of MCOP (Figure 3). The images given in figures 3a, 3b and 3c clearly indicate that the MCOP adopts a cauliflower-like morphology. These observations show that the substitution of cyanuric chloride and 4,4'-dihydroxybiphenyl leads to an uniform morphology, porosity and a certain degree of structural regularity. Figure 3d in the HR-TEM image clearly indicates the porosity of the structure.
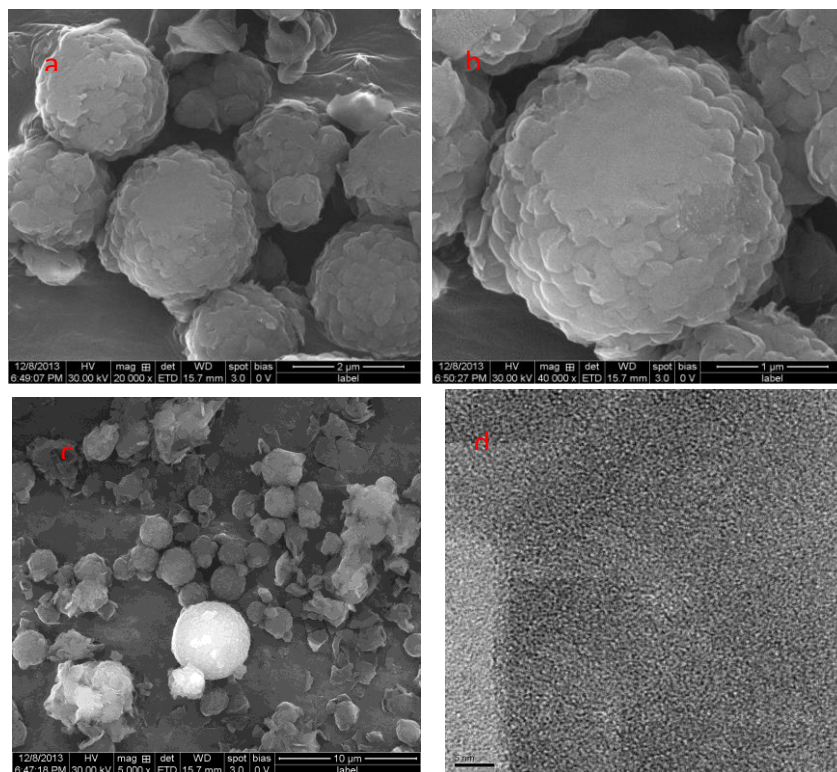
Fig. 3. Images of the synthesised MCOP (a, b and c are FE-SEM images and d is HR-TEM image of MCOP).

The regularity and crystallinity of the structure of MCOP material is further confirmed by powder XRD (Figure 4). The obtained PXRD pattern of MCOP indicates a partial crystallinity of the material and a set of peaks in the range of 8 to 35°, suggesting further that the framework of the material has certain degree of order.
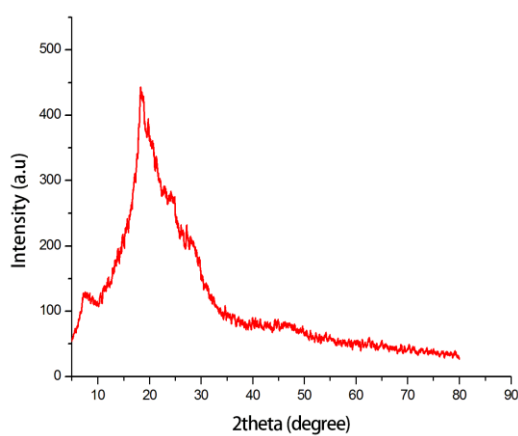
Fig. 4. Powder XRD pattern of MCOP

The thermal stability of MCOP was studied by thermogravimetric analysis (TGA) under nitrogen atmosphere (Figure 5). As shown in the figure 5, MCOP exhibits 3% weight loss around 80 ^{o}C due to loss of solvent molecules and the second weight loss takes place above 250 ^{o}C. A gradual weight loss (upto 60%) for MCOP was observed above 250 ^{o}C. The TGA of Pd@MCOP also represents good thermal stability upto 300 ^{o}C.
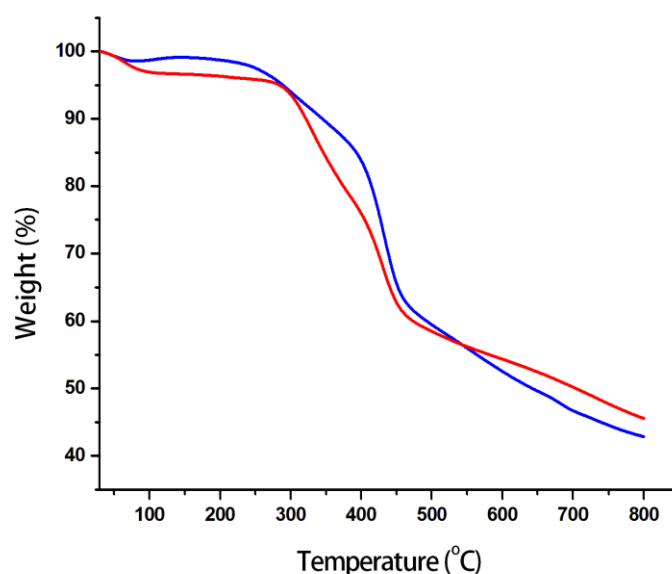
Fig. 5. TGA of MCOP (blue), Pd@MCOP (red)

The porosity and surface area of the above materials were measured by nitrogen adsorption-desorption analysis at 77 K (Figure 6). These isotherms are closely related to a type IV isotherm, which is characteristic of mesoporous materials.[4d,17] From the BET isotherms, the surface area is found to be 146 m^{2}g^{-1} for MCOP. Pore size distribution plots of MCOP (insets of figure 6) display a pore width of 23.4 Å.

8
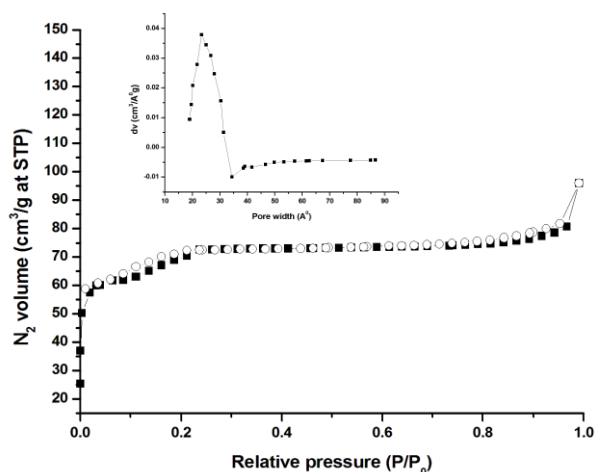
Fig. 6. Nitrogen adsorption-desorption isotherm of MCOP (adsorption-solid square, desorption-empty circle). Pore size distribution of MCOP (inset)

As seen from the structure of MCOP, which contains large amount of nitrogen and oxygen atoms, incorporation of suitable metal ions in its frameworks can be anticipated. Recently amorphous triazine based frameworks were successfully employed as heterogeneous supports for noble metal catalysts.[2a,5,12d] With this in mind, we have incorporated the Pd NPs on MCOP as supports (Pd@MCOP) which can serve as an excellent heterogeneous catalyst for Mizoraki-Heck cross coupling. Through a simple treatment of MCOP with palladium acetate, a Pd@MCOP material was synthesised in a facile manner (See supporting information). The synthesised Pd@MCOP was also characterized by powder XRD, HR-TEM, X-ray photoelectron spectroscopy (XPS) analysis and the stability of the material was confirmed by TGA. The palladium loading level of the fresh catalyst was found to be ~2.04 wt% from SEM-EDX and 2.42% from ICP-OES. The BET isotherm analysis shows a surface area of 63 m^2g^{-1} and almost no change in the pore size (23.2 Å) for Pd@MCOP.

9
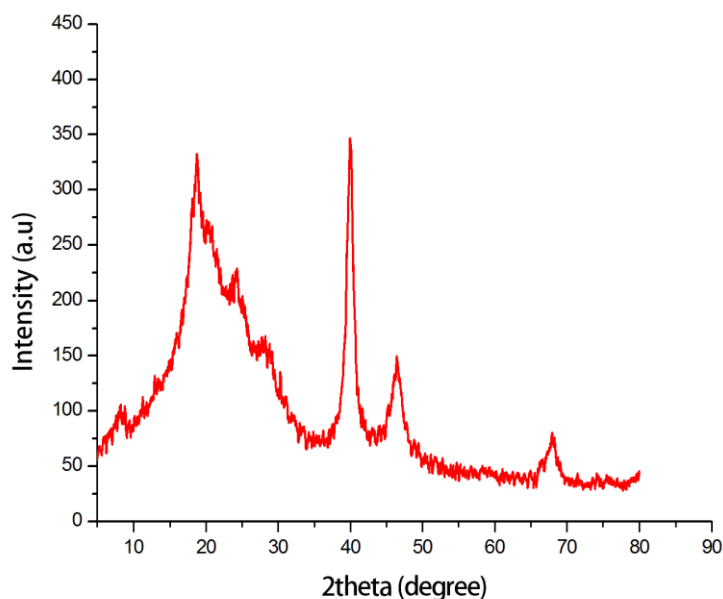
Fig. 7. Powder XRD pattern of Pd@MCOP

The crystalline nature of Pd NPs was confirmed from powder XRD data. Figure 7 shows the powder XRD pattern of the vacuum dried Pd@MCOP nanoparticles obtained from MCOP. A comparison of the powder XRD patterns of MCOP (Figure 4) and Pd@MCOP (Figure 7) shows that the structure of MCOP was well-kept-up after the synthesis of Pd NPs. Bragg reflections with 2θ values of 40.10^o, 46.42^o and 68.32^o corresponding to the (111), (200) and (220) sets of lattice planes are observed which may be indexed as the band for face centred cubic structures of palladium (JCPDS no. 7440-05-3). The PXRD pattern thus clearly illustrates the Pd NPs synthesized by the present method are crystalline in nature. The electronic state of palladium and the metallic palladium which was supported strongly on nitrogen of the MCOP materials were further confirmed by XPS analysis (Figure 8). XPS spectrum (Figure 8a) shows two strong peaks with binding energies at around 335.5 and 340.6 eV for the $3d_{5/2}$ and $3d_{3/2}$ core levels,[16,18] which clearly indicate that all the palladium species in Pd@MCOP catalyst exist in metallic state. In figure 8b of XPS spectrum, the N 1s core level of Pd@MCOP catalyst is described. The literature report of triazine unit (N 1s core

level) has binding energy of 398.9 eV.[19] The N 1s core level binding energy of Pd@MCOP catalyst appeared at 397.5 eV. This strong binding energy shift in the N 1s core level clearly demonstrates that the metallic palladium strongly binds with nitrogen of MCOP, which can stabilise the metallic palladium and can induce the catalytic performance of Pd@MCOP.
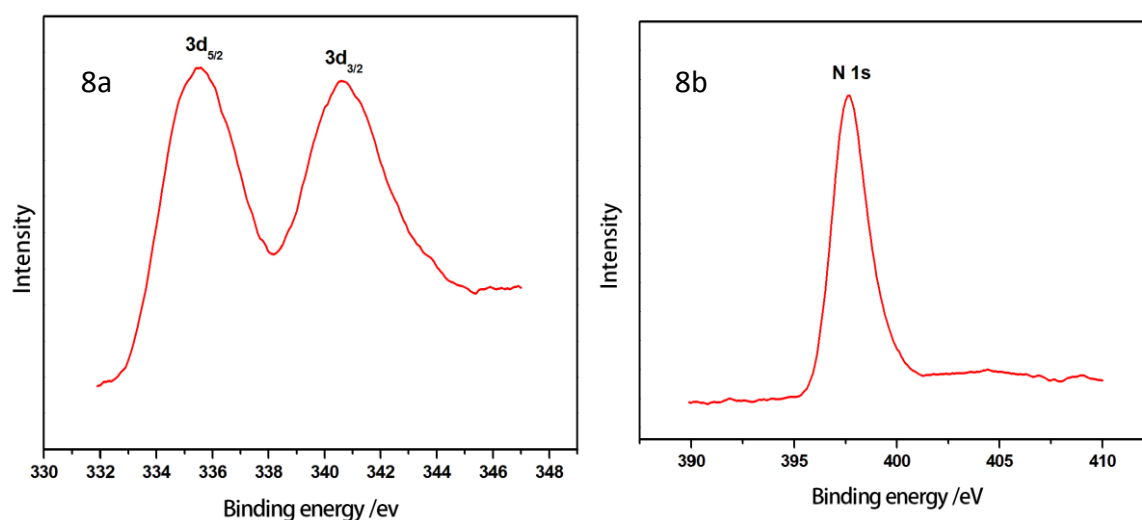
Fig. 8. XPS Spectra of fresh Pd@MCOP catalyst (a) metallic Pd species and (b) N 1s core levels

The HR-TEM analysis was used to determine the morphology and shape of Pd NPs supported on MCOP. The HR-TEM image analysis of the Pd@MCOP catalyst (Figure 9) suggested that the Pd NPs are in the 6-10 nm range and has almost spherical shapes. The catalytic activity of Pd@MCOP was examined in Mizoroki-Heck coupling reaction.
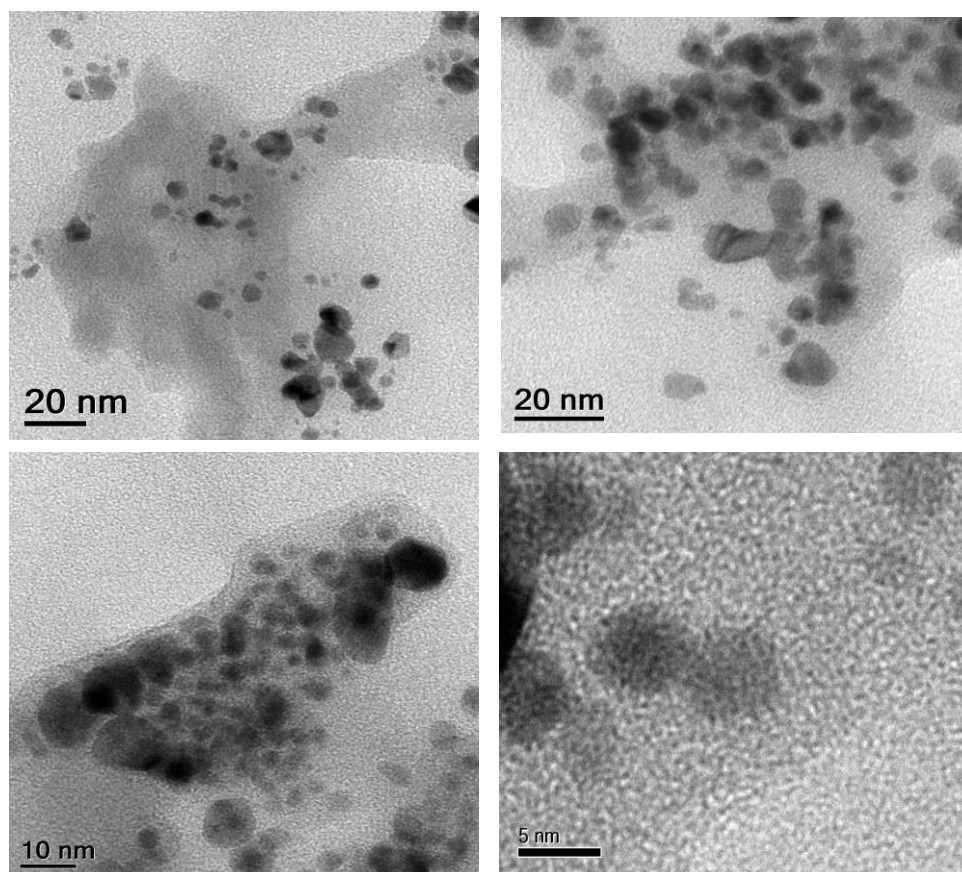
Fig. 9. HR-TEM image of the synthesised Pd@MCOP

The potential activity of Pd@MCOP is optimized in Mizoroki-Heck coupling reaction using the less reactive bromobenzene (1a) and styrene (2a) as model substrates and the results are summarized in table 1. In the absence of catalyst and in the presence of MCOP at 90 $^{\circ}$C, no product was obtained (Table 1, entries 1 and 2) and these results clearly highlight the specific role of palladium NPs as catalyst in the Mizoroki-Heck cross coupling reaction. Interestingly, when carried out with Pd@MCOP in DMF, the reaction became faster with a 94% yield of 3a, which indicates the importance of Pd NPs (Table 1, entry 3). The reaction was also conducted in *N,N'*-dimethyl acetamide (DMAc) and 90% yield of 3a was obtained (Table 1, entry 5). The reaction when studied in various solvents such as water, methanol, ethanol and acetonitrile, afforded only moderate yield (Table 1, entries 5 and 7-10). But with dimethyl sulfoxide as a solvent, the reaction proceeds smoothly with 97% yield (Table 1,

12

entry 6). On the other hand, use of mixture of solvents like DMSO:water (1:1), afforded 98%

yield (Table 1, entry 11). When the reaction was carried out with $Pd(OAc)_2$ instead of

Pd@MCOP, 57% yield of the product was observed (Table 1, entry 12). Among the various

inorganic and organic bases (Table 1, entries 13-16) used for this coupling reaction, K_2CO_3

gave excellent results.

Table 1. Optimization of reaction conditions.[a]
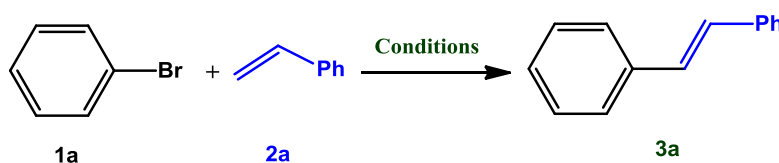
Entry	Catalyst	Base	Solvent	Temp. (^{o}C)	Yield (%)[b]
1	-	K_2CO_3	DMF	90	NR[f]
2	MCOP	K_2CO_3	DMF	90	NR[f]
3	Pd@MCOP	K_2CO_3	DMF	90	94
4	Pd@MCOP	-	DMF	90	NR[f]
5	Pd@MCOP	K_2CO_3	DMAc	90	90
6	Pd@MCOP	K_2CO_3	DMSO	90	97
7	Pd@MCOP	K_2CO_3	Water	90	57
8	Pd@MCOP	K_2CO_3	MeOH	90	62
9	Pd@MCOP	K_2CO_3	EtOH	90	60
10	Pd@MCOP	K_2CO_3	ACN	90	68
11	Pd@MCOP	K_2CO_3	DMSO:water[g]	90	98
12[c]	$Pd(OAc)_2$	K_2CO_3	DMSO:water[g]	90	57
13	Pd@MCOP	Na_2CO_3	DMSO:water[g]	90	92
14	Pd@MCOP	Cs_2CO_3	DMSO:water[g]	90	80
15	Pd@MCOP	K_3PO_4	DMSO:water[g]	90	83
16	Pd@MCOP	NEt_3	DMSO:water[g]	90	26
17	Pd@MCOP	K_2CO_3	DMSO:water[g]	100	98
18	Pd@MCOP	K_2CO_3	DMSO:water[g]	80	86
19	Pd@MCOP	K_2CO_3	DMSO:water[g]	70	79
20	Pd@MCOP	K_2CO_3	DMSO:water[g]	RT	NR
21[d]	Pd@MCOP	K_2CO_3	DMSO:water[g]	90	92
22[e]	Pd@MCOP	K_2CO_3	DMSO:water[g]	90	86

[a]Bromobenzene (1 mmol), styrene (1.2 mmol), base (1.5 mmol), solvent (2 mL), catalyst (30 mg, 0.006 mol%), 14 h; [b]Isolated yield based on bromobenzene; [c]5 mol% of $Pd(OAc)_2$; [d]Yield of the reaction carried out with 1 mmol of K_2CO_3; [e]Oxygen atmosphere; [f]NR = no reaction; [g]1:1 (v/v) ratio.

Under these conditions, the effect of other parameters such as temperature, amount of bases, catalyst and reaction time was also recorded. As a temperature below 90 ^{o}C, the yield of 3a decreased, whereas increasing the temperature above 90 ^{o}C (Table 1, entry 17-20) no marked change in overall yield is observed. The base concentration plays an important role in this heterogeneous palladium catalysed Mizoroki-Heck cross coupling reaction. In the absence of base, the reaction failed completely (Table 1, entry 4) and when the amount of base was reduced to 1 mmol, yield of 3a had reduced to 92%. (Table 1, entry 21). When the reaction was conducted in oxygen atmosphere, the Heck coupled product was observed in 86% yield along with 12% yield of Ullmann coupled product (Table 1, entry 22). As the amount of the solid (Pd@MCOP) catalyst was increased to 30 mg, the product was obtained in excellent yield and further addition of catalyst had no positive effect on the overall yield of the product (Figure 10). Increase of the reaction time from 2 to 10 h had increased the overall yield (Figure 11). These observations show that optimum conditions for this palladium catalysed Mizoroki-Heck coupling are use of Pd@MCOP (30 mg) as a catalyst in DMSO:water (1:1, v/v) at 90 °C with 1 mmol of base for 10 h.
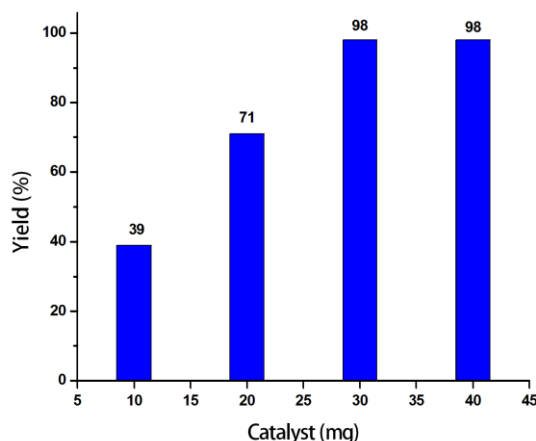
Fig. 10. Dependence of yield on amount of catalyst
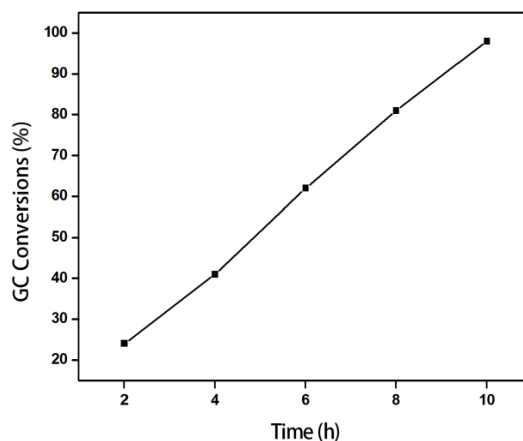
Fig. 11. Effect of reaction time on the percentage conversion in the Pd@MCOP catalysed Mizoroki-Heck reaction

The heterogeneity of the Pd@MCOP catalyst was checked by hot filtration test with bromobenzene and styrene as substrates, to find out whether Pd is leaching out from the solid catalyst to the solution or whether the catalyst is truly heterogeneous in nature. After continuing the reaction under optimized conditions for about 6 h, the catalyst was filtered in hot conditions from the reaction mixture with 62% formation of 3a (Table 2). After the removal of solid catalyst, the filtrate was then subjected to the reaction conditions for an additional 4 h.   After 10 h, no further yield of 3a was observed. The absence of any significant metal leaching was also confirmed from EDX. The EDX results suggested ~2.04 wt% and ~2.00 wt% of palladium in fresh and fifth reused Pd@MCOP (See supporting informations figures S1, S2 and tables S1, S2). ICP analysis of the filtrate from the hot mixture showed the presence of 0.003% of the palladium in the solution and in the reused Pd@MCOP (after fifth reuse), the palladium content is found to be 2.41%. These results demonstrate clearly that Pd@MCOP is truly heterogeneous in nature.

15

Table 2. Hot filtration test

Catalyst	GC Conversion (%)	
Pd@MCOP	**6 h**	**(6+4) h**
	62	62

[a]Bromobenzene (1 mmol), Styrene (1.2 mmol, 1.2 equi.), K_2CO_3 (1.5 equi.), DMSO:water (2 mL, 1:1, v/v), Pd@MCOP (30 mg, 0.006 mol%), 90 ^{o}C, 10 h.

After identifying the optimal conditions for the Mizoroki-Heck reactions catalysed by Pd@MCOP, the activity of a range of alkenes and substituted aryl bromides was also evaluated and the results are summarized in table 3. It was observed that the aryl bromides containing electron-withdrawing group coupled readily with styrene to give excellent yields. Examples include 4-bromonitrobenzene, 4'-acetylbromobenzene, 4-bromobenzonitrile, 4-fluoro-1-bromobenzene, 4-chloro-1-bromobenzene and 3,5-dichloro-1-bromobenzene (Table 3, entries 4-8 and 11). Interestingly, coupling of aryl bromides bearing a methyl or methoxy group with styrene also gave higher yields (Table 3, entries 3, 4 and 9). The reaction was also facile with sterically hindered substrates such as 2-bromo-4-nitrotoluene, 2-bromonitrobenzene (Table 3, entries 14 and 15), although a longer reaction time (16 h) was required. It should also be noted that aryl bromides can be selectively coupled in the presence of aryl chlorides. When the substrate contains both bromo and chloro substituents, styrene coupled readily only with the bromo side (Table 3, entry 8). 1,3,5-Tribromobenzene was also successfully coupled with styrene in good yield (Table 3, entry 16), although a longer reaction time (16 h) was required. Heteroaromatic and bicyclic bromides also gave the corresponding coupled products in excellent yields (Table 3, entries 12, 17-20). Different substituted aromatic alkenes (Table 3, entries 21-25) and heteroaromatic alkenes (Table 3, entry 26) also afforded good to excellent yields.

16

Table 3. Mizoroki-Heck reaction catalyzed by Pd@MCOP with different substituents.[a]
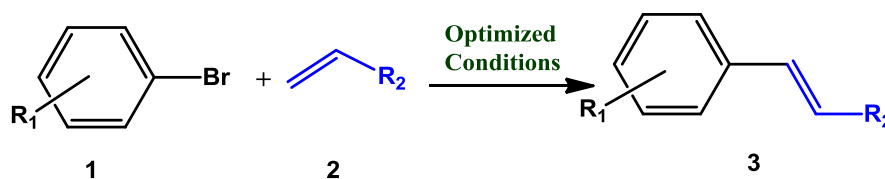
Entry	Aryl bromides (1)	Alkenes (2)	(3)	Yield (%)[b]
1	Bromobenzene	Styrene	**3a**	98
2	4-Bromoanisole	Styrene	**3b**	95
3	4-Bromotoluene	Styrene	**3c**	94
4	4-Bromonitrobenzene	Styrene	**3d**	91
5	4'-Acetylbromobenzene	Styrene	**3e**	90
6	4-Bromobenzonitrile	Styrene	**3f**	89
7	4-Fluorobromobenzene	Styrene	**3g**	93
8	4-Chlorobromobenzene	Styrene	**3h**	94
9	3-Bromoanisole	Styrene	**3i**	91
10	3,5-Dimethoxybromobenzene	Styrene	**3j**	93
11	3,5-Dichlorobromobenzene	Styrene	**3k**	86
12	1-Bromonaphthalene	Styrene	**3l**	90
13	2-Fluoro-4-bromoanisole	Styrene	**3m**	91
14[c]	2-Bromo-4-nitrotoluene	Styrene	**3n**	87
15[c]	2-Bromonitrobenzene	Styrene	**3o**	84
16[c]	1,3,5-Tribromobenzene	Styrene	**3p**	80
17	3-Bromopyridine	Styrene	**3q**	93
18	3-Bromothiophene	Styrene	**3r**	96
19	2-Bromothiophene	Styrene	**3s**	95
20[c]	3-Hexyl-2-bromothiophene	Styrene	**3t**	82
21	Bromobenzene	4-Methoxystyrene	**3b**	92
22	Bromobenzene	4-Methylstyrene	**3c**	91
23	4-Bromotoluene	4-Methoxystyrene	**3u**	90
24	4-Bromoanisole	4-Methoxystyrene	**3v**	93
25	Bromobenzene	4-Vinylbenzoic acid	**3w**	87
26[c]	4-Bromotoluene	4-Methyl-5-vinylthiazole	**3x**	88
27	Bromobenzene	Methylacrylate	**3y**	94

[a]Aryl bromides (1 mmol), alkenes (1.2 mmol, 1.2 equi.), K_2CO_3 (1.5 equi.), DMSO:water (2 mL, 1:1, v/v), Pd@MCOP (30 mg, 0.006 mol%), 90 ^{o}C, 10 h. [b]Isolated yield based on aryl bromides. [c]16 h.

One of the main advantages of using heterogeneous catalysts such as Pd@MCOP from an industrial perspective is that they can be recovered and reused efficiently upto eight consecutive runs. After completion of the reaction, the solid catalyst was recovered by filtration and extensively washed with ethyl acetate and dried at room temperature in a vacuum desiccator for 2 h. Upto five consecutive reactions, only a marginal loss in the activity of the catalyst is observed and from the sixth to eighth runs, the decrease in activity is small, yet significant (Figure 12).
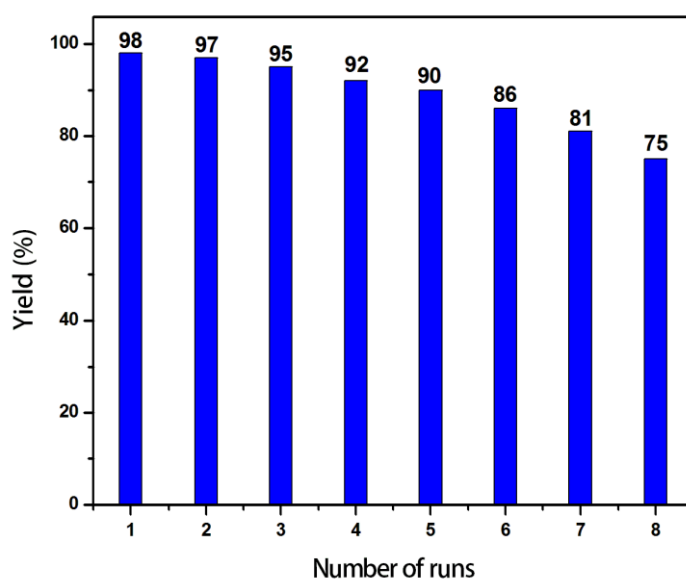
Fig. 12. Recycling of the Pd@MCOP catalyst

On the basis of the above results, and also in accordance with previous literature reports,[11-13] a plausible reaction pathway is proposed as shown in Scheme 2. In the first step, oxidative addition of aryl bromides to Pd(0) leads to a Pd(II) species. In the second step, the alkene coordinates to Pd(II) species, which then undergoes an insertion reaction to form the Pd(II) complex. The coupled aryl and alkenic compounds of palladium(II) complex is then eliminated *via* a *β*-hydride removal followed by reductive elimination with base to retain the original Pd(0).
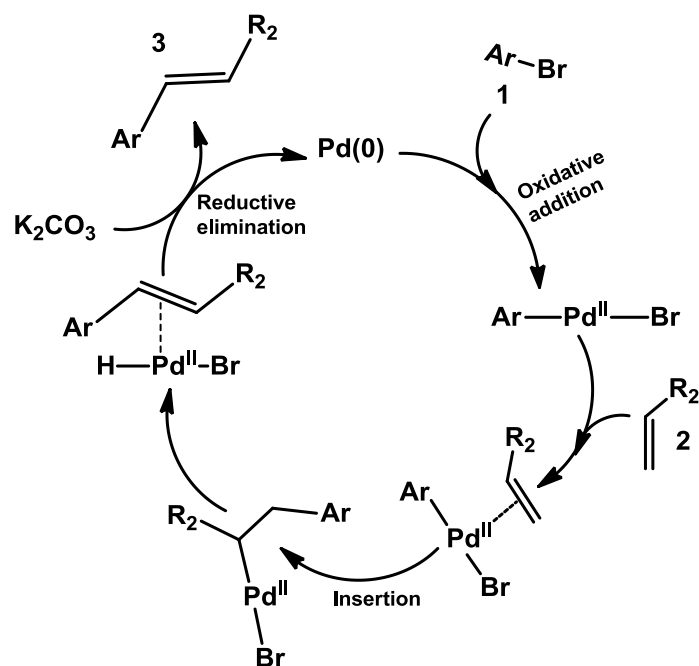
Scheme 2. Plausible mechanistic pathway of Mizoroki-Heck reaction

Data on reaction conditions, activity and efficiency of the various other catalysts employed earlier for the Mizoroki-Heck cross coupling of aryl bromides with styrene are given in Table 4. Comparison of the results indicates that our catalytic system (entry 22) exhibits better catalytic activity compared to other reported catalysts. These systems require external additives (entries 4, 13, 16 and 21), an inert atmosphere (entries 1, 3 and 13), longer reaction time (entries 2, 6, 7, 11 and 16-20) and higher temperature (entries 1-21).

19

Table 4: Comparison with previously reported catalytic systems for the Mizoroki-Heck cross coupling of aryl bromides with styrene

Entry	Catalyst	Additive	Base	Solvent	Atm.	Temp. (^{o}C)	Time (h)	Yield (%)	References
1	[Pd{P(o-Tol)$_3$}$_2$]	-	NaOAc	DMF	N$_2$	130 ^{o}C	10h	94	20
2	CB[6]–Pd NPs	-	Na$_2$CO$_3$	DMF	-	140 ^{o}C	24h	82	12f
3	Pd-TPA/ZrO$_2$	-	K$_2$CO$_3$	DMF	N$_2$	120 ^{o}C	6h	59	21
4	Cyclopalladated ferrocenyl imine	TBAB	K$_3$PO$_4$	DMF	-	140 ^{o}C	5h	96	22
5	Pd/MIL-53(Al) and 50 % NH$_2$	-	TEA	DMF	-	120 ^{o}C	6h	93	12a
6	K-Pd-Me$_{10}$-CB	-	Na$_2$CO$_3$	DMF	-	140 ^{o}C	24h	84	23
7	Pd/C	-	NaOAc	DMAc		140 ^{o}C	24h	84	24
8	SPIONs-*bis*(NHC)-palladium(II)	-	K$_2$CO$_3$	DMF	Air	90 ^{o}C	6h	82	25
9	[Pd{C6H2(CH2 CH2NH2)-(OMe)$_2$,3,4}Br(PPh3)]	-	K$_2$CO$_3$	NMP	-	130 ^{o}C	1h	92	26
10	[Pd(PhP(C6H4 -2-S)$_2$)(PAr$_3$)]	-	Cs$_2$CO$_3$	DMF	-	160 ^{o}C	4h	85	27
11	Seven membered phosphine ylied palladacycle	-	K$_2$CO$_3$	NMP	Air	130 ^{o}C	24h	90	28
12	PNP–SSS	-	K$_2$CO$_3$	Water	-	Reflux	5h	92	29
13	Palladium dichloro-bis(aminophosphine) complexes	TBAB	K$_2$CO$_3$	NMP	N$_2$	100 ^{o}C	14h	92	30
14	NHC–palladium complexes	-	K$_2$CO$_3$	NMP	Air	105 ^{o}C	10h	85	31
15	POM-IL-Pd	-	TEA	DMF	-	100 ^{o}C	2h	49	32
16	PdCl$_2$(DBPF)2	TBAC	Cy$_2$NMe	DMAc	-	80 ^{o}C	24h	99	33
17	Pd^0/SiO2	-	Na$_2$CO$_3$	DMAc	Ar	135 ^{o}C			34
18	Pd(0)-MCM-41	-	NaOAc	DMF	-	100 ^{o}C	24h	56	35
19	NHCs-Pd	-	KOAc	DMAc	-	140 ^{o}C	24h	87	36
20	Pd(OAc)$_2$	-	K$_3$PO$_4$	DMAc	-	140 ^{o}C	25h	98	37
21	PdCl$_2$	GIL2	-	-	-	140 ^{o}C	1h	96	38
22	**Pd@MCOP**	**-**	**K$_2$CO$_3$**	**DMSO: water (v/v)**	**-**	**90 ^{o}C**	**10h**	**98**	**Present work**

CB = Cucurbituril; TPA = 12-tunstophosphoric acid; MIL = Materials of the Institute Lavoisier; SPIONs = SuperParamagnetic Iron Oxide Nanoparticles; SSS = Silica Starch Subsrate; POM-IL = Polyoxometalate-Ionic Liquid; DBPF = di-bisphosphenylferrocene; TBAB = tetrabutylammonium bromide; TBAC = tetrabutylammonium chloride; MCM = Mesoporous silica matrix; GIL = Guanidine based ionic liquids.

Experimental Section

General Methods

All chemicals were purchased from commercial suppliers and used without further purification as commercially available unless otherwise noted. Solvents were dried and distilled through standard procedure. NMR spectra were recorded at 400 and 300 MHz (mentioned in respective NMR data itself) on Brucker spectrometer. All ^{1}H NMR and ^{13}C NMR spectra were measured in $CDCl_3$ with TMS as the internal standard. The powder XRD pattern of the catalyst sample was measured with a SHIMADZU XD-D1 using a Cu Kα radiation at room temperature. ^{13}C soild state cross polarization magic angle spinning nuclear magnetic resonance (CP-MAS NMR) measurements were carried out using a Bruker Avance 300 spectrometer operating at 75 MHz for carbon NMR. Brunauere Emmette Teller (BET) surface area analysis was carried out using the Quantachrome-Autosorb at 77K. Surface morphology and microstructures of the materials were analysed using the field emission scanning electron microscopy (FESEM) on a SFG (Quanta-250) instrument. High resolution transmission electron microscopy (HRTEM) images were recorded with a FEI TECNAI 30 G^2 S-TWIN instrument. EDX analysis of the materials was analysed using the scanning electron microscopy energy dispersive X-ray on a HITACHI S-3400N instrument. IR spectral analyses were performed using JASCO FT/IR-410 instrument by KBr pellet technique in the range of 4000-500 cm^{-1}. Thermogravimetric analysis (TGA) was performed with a TGA/ Shimadzu Thermal Analyser under nitrogen atmosphere in the temperature range 30–800 ^{o}C in a flow of nitrogen at a heating rate of 10 ^{o}C min^{-1}. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Kratos AXIS Ultra DLD X-ray photoelectron spectrometer with a monochromatic Al Kα X-ray source and a hemispherical analyser. Base pressure in the analysis chamber was maintained in the range of 1 x10^{-8} Torr. The Pd contents

of the Pd@COF samples were determined by ICP-OES analysis with an Perkin Elmer Optima 5300 DV instrument.

Synthesis of MCOP

A round-bottom flask fitted with a condenser, cyanuric chloride 0.8 mmol) was dissolved in 10 mL of dioxane at 0 ^{o}C. Then the 4,4'-dihydroxybiphenyl (1.2 mmol) and *N,N*-diisopropyl ethylamine (1.5 mmol) were added to round bottom flask. After stirred at 0 ^{o}C for 2 h, the temperature was raised to room temperature and then refluxed for 1 day. After 1 day, reaction mixture was then cooled and the solid was removed by filtration and washed with hot ethyl acetate and 20 mL of 10% Na_2CO_3 (twice) and then the solid was immersed in ethyl acetate for 3 days.

Synthesis of Pd@MCOP

In a typical experiment, a mixture of palladium acetate (30 mg) in acetone and MCOP material (500 mg) was stirred at room temperature for 48 h. After 48 h, the solid was filtered and washed with acetone and methanol to remove any unreacted palladium acetate. The freshly prepared Pd/MCOP (500 mg) was added to 50 mL of water, and the mixture was stirred for 10 min. Then hydrazine hydrate (2 mL, excess) was added dropwise to the suspension under vigorously stirring, and the mixture turned to gray immediately. After stirring for 10 min, the solid was isolated by filtration, washed with water, Pd@MCOP was obtained as brown powder, and kept under nitrogen atmosphere.

22

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General procedure for Mizoroki-Heck cross coupling reaction between aryl bromides and alkenes

An reaction tube equipped with a magnetic stirring bar was charged with Pd@MCOP (0.006 mol% of palladium loaded in 30 mg), aryl bromides (1.0 mmol), alkenes (1.2 mmol), K_2CO_3 (1.5 mmol) and DMSO:Water (2.0 mL, 1:1, v/v). Then the mixture was allowed to stir at 90 ^{o}C for a certain time. After completion of the reaction, the reaction mixture was cooled down to room temperature, treated with ethyl acetate (10 mL), the catalyst was filtered and the filtrate was extracted with distilled water, and organic layer was dried over anhydrous sodium sulfate. After the organic solvent was evaporated in vacuum, the residues were purified by passive over a column of silica gel (60-120 mesh) afforded the corresponding pure coupled product. The recovered catalyst was thoroughly washed with ethylacetate and activated under vacuum at room temperature for 1 h, which was subsequently reused.

Conclusions

In summary, we have developed a novel nitrogen rich functional mesoporous covalent organic polymer which functions as good support for palladium nanoparticles (Pd@MCOP) as a heterogeneous catalyst with excellent catalytic activity in Mizoroki-Heck cross coupling reaction of aryl bromides and alkenes under mild conditions. A variety of aryl bromides and alkenes were reacted in good to excellent yields. In addition, the Pd@MCOP was also attractive in view of its low cost, easy synthesis and it is also environmentally friendly, highly stable, show negligible metal leaching and can be reused under optimal conditions with only minor loss in its catalytic activity. Thus the present nitrogen rich functional material can serve as an excellent mesoporous support and can potentially find extensive catalytic applications in industries.

Acknowledgements

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