Green Chemistry

PAPER

Cite this: DOI: 10.1039/c4qc00412d

Received 8th March 2014, Accepted 9th June 2014 DOI: 10.1039/c4gc00412d

www.rsc.org/greenchem

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 those 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, COPs based materials have found various applications of technical relevance in separation, gas storage, gas purification, drug delivery, sensors, semiconductive and photoconductive devices, charge carriers and catalysis.⁴ Consequently the inclusion of multifaceted functionality into porous networks is one of the frontline areas of research, which could lead to the synthesis of new materials with diverse applications. For example, the 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

Palladium nanoparticles supported on triazine functionalised mesoporous covalent organic polymers as efficient catalysts for Mizoroki–Heck cross coupling reaction[†]

Pillaiyar Puthiaraj^a and Kasi Pitchumani*^{a,b}

A novel class of mesoporous covalent organic polymer (MCOP) was synthesised by the nucleophilic substitution of cyanuric chloride with 4,4'-dihydroxybiphenyl. The MCOP was fully characterized using powder X-ray diffraction analysis, Fourier transform infrared spectroscopy, ¹³C-solid state NMR spectroscopy, field emission scanning electron microscopy and thermogravimetric analysis. These nitrogen rich materials act as good supports for palladium nanoparticles (Pd NPs) and exhibit 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 polymers are also cheap, easy to synthesise and can be recycled up to five times with only a minor loss of activity.

Recently, we have reported triazine based mesoporous covalent imine polymers as novel solid supports for copper mediated Chan–Lam cross coupling of the N-arylation reaction.^{5b} Some 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 organic solvents, tedious synthetic protocols are needed for their synthesis as well as the usage of these catalysts.⁷ In order to overcome these issues, we believe that the synthesis is desirable of new highly stable porous materials in which there is a strong interaction between the support and the loaded metals.

The 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 for new derivatives with wide ranging therapeutic potentials.^{8,9} Over the decades, various homogeneous catalytic systems, which always exhibit better activity and selectivity, have been developed for this transformation.¹⁰ Although many organometallic compounds with special ligands have been used as catalysts for 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, the potential application of homogeneous catalytic systems in industry is limited due to difficulties in separation, recovery and reusability and metal leaching of these expensive catalysts.¹¹ Thus the current challenge for palladium catalyzed coupling reactions is the

Published on 12 June 2014. Downloaded by Dalhousie University on 14/07/2014 20:56:33.



^aSchool of Chemistry, Madurai Kamaraj University, Madurai-625 021, India ^bCentre for Green Chemistry Processes, School of Chemistry, Madurai Kamaraj University, Madurai-625021, India. E-mail: pit12399@yahoo.com

[†]Electronic supplementary information (ESI) available. See DOI: 10.1039/c4gc00412d

Paper

development of high performance catalysts using sustainable and environmentally benign reaction conditions.¹² Thus, the search for heterogeneous technologies that are greener, safer, environmentally friendly and reusable is a research priority, particular for the chemical and pharmaceutical industries. Recently, our group reported the use of a palladium aminocyclodextrin complex as an efficient catalyst for Heck cross coupling.¹³ However, palladium nanoparticles (Pd NPs), which are important heterogeneous catalysts, are prone to aggregation 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 catalysts 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 suitable supports for Pd NPs catalysts is an important goal in heterogeneous catalysis. Recently, Zhang et al. have reported the use of mesoporous silica supported Pd NPs as an efficient and reusable catalyst for the 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 polymer supported Pd NPs for use in the Heck reaction under eco-friendly conditions. The porous organic polymer materials have been synthesised by means of the simple nucleophilic substitution of relatively cheap, industrially important and readily accessible chemicals.

Results 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 spectroscopy (FT-IR), ¹³C cross polarization-magic angle spinning (CP-MAS) NMR spectroscopy, field emission-scanning electron microscopy (FE-SEM), powder X-ray diffraction analysis (PXRD), 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*.

The bands at 1249 cm^{-1} and 1562 cm^{-1} in the FT-IR spectrum of MCOP (Fig. 1) indicate the presence of C–O–C bonds and triazine units. The C–Cl stretching at 851 cm^{-1} has completely diminished, suggesting that the starting material, cyanuric chloride, has been converted.

The CP-MAS NMR spectral data (Fig. 2) clearly confirmed the chemical structure of the synthesised MCOP material. Five peaks at 122.2, 127.1, 137.4, 151.4, 173.5 ppm can be seen in the solid state NMR spectrum. The peak at 173.5 ppm corres-



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



Scheme 1 Schematic representation of MCOP.



ponds to the triazine carbon. The peak at 151.4 ppm corresponds to the carbon atom of the oxygen attached to 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.

The morphology and porosity of MCOP can be observed from the FE-SEM and high resolution-transmission electron microscopy (HR-TEM) images presented in Fig. 3. The images presented in Fig. 3a–3c clearly indicate that MCOP adopts a cauliflower-like morphology. These observations show that the substitution of cyanuric chloride and 4,4'-dihydroxybiphenyl leads to a uniform morphology, porosity and a certain degree of structural regularity. Fig. 3d in the HR-TEM image clearly indicates the porosity of the structure.

The regularity and crystallinity of the structure of the MCOP material was further confirmed by PXRD (Fig. 4). The obtained PXRD pattern of MCOP indicates the partial crystallinity of the material, furthermore, the set of peaks in the range of 8 to 35°



Fig. 4 Powder XRD pattern of MCOP.



Fig. 3 Images of the synthesised MCOP (a, b and c are FE-SEM images and d is an HR-TEM image of MCOP).

suggests that the framework of the material has a certain degree of order.

The thermal stability of MCOP was studied by TGA under a nitrogen atmosphere (Fig. 5). As shown in Fig. 5, MCOP exhibits a 3% weight loss at around 80 °C due to the loss of solvent molecules and the second weight loss takes place above 250 °C. A gradual weight loss (up to 60%) of MCOP was observed above 250 °C. The TGA of Pd@MCOP demonstrated that it also had good thermal stability up to 300 °C.

The porosity and surface area of the above materials were measured by nitrogen adsorption–desorption analysis at 77 K (Fig. 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 was found to be 146 m² g⁻¹ for MCOP. Pore size distribution plots of MCOP (insets of Fig. 6) display a pore width of 23.4 Å.





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 amounts of nitrogen and oxygen atoms, the 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 incorporated the Pd NPs on MCOP as a support (Pd@MCOP) for use as an excellent heterogeneous catalyst for Mizoroki-Heck cross coupling. Through the simple treatment of MCOP with palladium acetate, a Pd@MCOP material was synthesised in a facile manner (see ESI[†]). The synthesised Pd@MCOP was also characterized by PXRD, 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-energy dispersive X-ray spectroscopy (EDX) and 2.42% from inductively coupled plasma-optical emission spectroscopy (ICP-OES). From BET isotherm analysis of Pd@MCOP the surface area was found to be 63 m² g⁻¹ and there was almost no change in the pore size (23.2 Å).

The crystalline nature of the Pd NPs was confirmed from PXRD data. Fig. 7 shows the PXRD pattern of vacuum dried Pd@MCOP NPs obtained from MCOP. A comparison of the PXRD patterns of MCOP (Fig. 4) and Pd@MCOP (Fig. 7) shows that the structure of MCOP was well maintained after the synthesis of Pd NPs. Bragg reflections with 2θ values of 40.10°, 46.42° and 68.32° 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 that 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 the nitrogen in the MCOP materials were further confirmed by XPS analysis (Fig. 8). 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 can be



Fig. 7 Powder XRD pattern of Pd@MCOP

Paper



Fig. 8 XPS spectra of fresh Pd@MCOP catalyst (a) metallic Pd species and (b) N 1s core levels.

seen in the XPS spectrum presented in Fig. 8a,^{16,18} which clearly indicates that all of the palladium species in Pd@MCOP catalyst exist in the metallic state. Fig. 8b is an XPS spectrum describing the N 1s core level of Pd@MCOP catalyst. A binding energy of 398.9 eV has been previously reported for the triazine unit (N 1s core level).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, thereby stabilising the metallic palladium and inducing the catalytic performance of Pd@MCOP.

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 (Fig. 9) suggested that the



Fig. 9 HR-TEM image of the synthesised Pd@MCOP.



Entry	Catalyst	Base	Solvent	(°C)	(%)
1	_	K ₂ CO ₃	DMF	90	NR^{f}
2	MCOP	K ₂ CO 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 K₂CO₃. ^{*e*} Oxygen atmosphere. ^{*f*} NR = no reaction. ^{*g*} 1 : 1 (v/v) ratio.

Pd NPs are in the 6–10 nm range and have almost spherical shapes. The catalytic activity of Pd@MCOP was examined in the Mizoroki–Heck coupling reaction.

The potential activity of Pd@MCOP was optimized for the 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 °C, no product was obtained (Table 1, entries 1 and 2) and these results clearly highlight the specific role of palladium NPs as catalysts in the Mizoroki-Heck cross coupling reaction. Interestingly, when the reaction was carried out with Pd@MCOP in DMF, it was 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 was studied in various solvents such as water, methanol, ethanol and acetonitrile, only moderate yields were afforded (Table 1, entries 5 and 7-10). But with dimethyl sulfoxide as a solvent, the reaction proceeded smoothly with 97% yield (Table 1, entry 6). On the other hand, use of a 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, a 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.

Under these conditions, the effect of other parameters such as temperature, amount of bases, catalyst and reaction time was also recorded. At a temperature below 90 °C, the yield of 3a decreased, whereas an increase of the temperature to above 90 °C (Table 1, entries 17-20) resulted in no marked change in the overall yield. 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, the yield of 3a was reduced to 92% (Table 1, entry 21). When the reaction was conducted in an oxygen atmosphere, the Heck coupled product was observed with an 86% yield along with a 12% yield of the 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 (Fig. 10). An increase of the reaction time from 2 to 10 h increased the overall yield (Fig. 11). These observations show that the 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.

The heterogeneity of the Pd@MCOP catalyst was checked by carrying out a 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 under hot conditions from the reaction mixture with 62% formation of **3a** (Table 2). After removal of the 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 by EDX. The EDX results suggested \sim 2.04 wt% and \sim 2.00 wt% of palladium in fresh and fifth reused Pd@MCOP (see ESI Fig. S1, S2 and Tables S1, S2†). ICP



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.

 Table 2
 Hot filtration test^a

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

 a Bromobenzene (1 mmol), Styrene (1.2 mmol, 1.2 equiv.), $K_2 CO_3$ (1.5 equiv.), DMSO-water (2 mL, 1:1, v/v), Pd@MCOP (30 mg, 0.006 mol%), 90 °C, 10 h.

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 was found to be 2.41%. These results clearly demonstrate that Pd@MCOP is truly heterogeneous in nature.

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 groups 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 any 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

Table 3 Mizoroki–Heck reaction catalyzed by Pd@MCOP with different substituents^a

R1	Br + R ₂	Optimized Conditions		—R ₂
	1 2		3	
Entry	Aryl bromides (1)	Alkenes (2)	(3)	Yield ^{&} (%)
$ \begin{bmatrix} 1 \\ 2 \end{bmatrix} $ $ \begin{bmatrix} 3 \\ 5 \end{bmatrix} $ $ \begin{bmatrix} 7 \\ 3 \end{bmatrix} $ $ \begin{bmatrix} 1 \\ 12 \\ 13 \\ 14^c \\ 15^c \end{bmatrix} $	Bromobenzene 4-Bromoanisole 4-Bromonitrobenzene 4'-Acetylbromobenzene 4'-Bromobenzonitrile 4-Fluorobromobenzene 3-Bromoanisole 3,5-Dimethoxy- bromobenzene 3,5-Dichlorobromobenzene 1-Bromonaphthalene 2-Fluoro-4-bromoanisole 2-Bromo-4-nitrotoluene 2-Bromonitrobenzene	Styrene Styrene Styrene Styrene Styrene Styrene Styrene Styrene Styrene Styrene Styrene Styrene Styrene Styrene Styrene Styrene Styrene	3a 3b 3c 3d 3e 3f 3g 3h 3i 3j 3k 3l 3m 3n 30	98 95 94 91 90 89 93 94 91 93 86 90 91 87 84
16° 17 18 19 20° 21 22 23 24 25 26° 27	 2 Bontonintroochizene 1,3,5-Tribromobenzene 3-Bromopyridine 3-Bromothiophene 2-Bromothiophene 3-Hexyl-2-bromothiophene Bromobenzene 4-Bromotoluene 4-Bromotoluene 4-Bromotoluene Bromobenzene Bromobenzene 	Styrene Styrene Styrene Styrene 4-Methoxystyrene 4-Methoxystyrene 4-Methoxystyrene 4-Methoxystyrene 4-Vinylbenzoic acid 4-Methyl- 5-vinylthiazole Methylacrylate	3p 3q 3r 3s 3t 3b 3c 3u 3v 3w 3x 3y	80 93 96 95 82 92 91 90 93 87 88 94



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.

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 up to 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. Only a marginal loss in the activity of the catalyst was observed for up to five consecutive reactions, and from the sixth to eighth runs, the decrease in activity was small, yet significant (Fig. 12).

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 $Pd(\pi)$ species. In the second step, the alkene coordinates to $Pd(\pi)$ species, which then undergoes an insertion reaction to form



Fig. 12 Recycling of the Pd@MCOP catalyst.



Scheme 2 Plausible mechanistic pathway forthe Mizoroki-Heck reaction.

the $Pd(\pi)$ complex. The coupled aryl and alkenic compound of the palladium(π) complex is then eliminated *via* a β -hydride removal followed by reductive elimination with base to retain the original Pd(0).

Details of the 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).

Experimental section

General methods

All of the chemicals were purchased from commercial suppliers and used without further purification as commercially available unless otherwise noted. Solvents were dried and distilled following a standard procedure. NMR spectra were recorded at 400 and 300 MHz (mentioned in the respective NMR data) using a Brucker spectrometer. All of the ¹H NMR and ¹³C NMR spectra were measured in CDCl₃ with TMS as the internal standard. The PXRD pattern of the catalyst sample was measured with a SHIMADZU XD-D1 instrument using Cu Ka radiation at room temperature. CP-MAS NMR measurements were carried out using a Bruker Avance 300 spectrometer operating at 75 MHz for carbon NMR. Brunauer Emmett Teller (BET) surface area analysis was carried out using a Ouantachrome-Autosorb instrument at 77 K. Surface morphology and microstructures of the materials were analysed by FESEM on a SFG (Quanta-250) instrument. HRTEM images were recorded with a FEI TECNAI 30 G² S-TWIN instrument. SEM-EDX analysis of the materials was carried out using an HITACHI S-3400N instrument. IR spectral analyses were performed using a JASCO FT/IR-410 instrument in the range of 4000–500 cm⁻¹ and the KBr pellet technique. TGA was performed with a TGA/Shimadzu Thermal Analyser under a nitrogen atmosphere in the temperature range 30-800 °C at a heating rate of 10 °C min⁻¹. XPS measurements were performed using a Kratos AXIS Ultra DLD X-ray photoelectron spectrometer with a monochromatic Al Ka X-ray source and a hemispherical analyser. Base pressure in the analysis chamber was maintained in the range of 1×10^{-8} Torr. The Pd contents of the Pd@COF samples were determined by ICP-OES analysis with a Perkin Elmer Optima 5300 DV instrument.

Synthesis of MCOP

Cyanuric chloride (0.8 mmol) was dissolved in 10 mL of dioxane at 0 °C in a round-bottomed flask fitted with a condenser. Then 4,4'-dihydroxybiphenyl (1.2 mmol) and *N*,*N*-diisopropyl ethylamine (1.5 mmol) were added to the round-bottomed flask. After stirring at 0 °C for 2 h, the temperature was raised to room temperature and then refluxed for 1 day. After 1 day, the reaction mixture was cooled and the solid was removed by filtration and washed with hot ethyl acetate and 20 mL of 10% Na₂CO₃ (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 vigorous stirring, and the mixture turned gray immediately. After stirring for 10 min, the

	Table 4	Comparison with	n previously reporte	d catalytic systems f	or the Mizoroki–Heck cross	s coupling of aryl bro	mides with styrene
--	---------	-----------------	----------------------	-----------------------	----------------------------	------------------------	--------------------

Entry	Catalyst	Additive	Base	Solvent	Atm.	Temp. (°C)	Time (h)	Yield (%)	References
1	$[Pd{P(o-Tol)_3}_2]$	_	NaOAc	DMF	N_2	130 °C	10 h	94	20
2	CB[6]–Pd NPs	—	Na_2CO_3	DMF	—	140 °C	24 h	82	12f
3	Pd-TPA/ZrO ₂	_	K_2CO_3	DMF	N_2	120 °C	6 h	59	21
4	Cyclopalladated ferrocenyl imine	TBAB	K_3PO_4	DMF		140 °C	5 h	96	22
5	Pd/MIL-53(Al) and 50% NH ₂		TEA	DMF		120 °C	6 h	93	12 <i>a</i>
6	K-Pd-Me ₁₀ -CB		Na_2CO_3	DMF		140 °C	24 h	84	23
7	Pd/C		NaOAc	DMAc		140 °C	24 h	84	24
8	SPIONs-bis(NHC)-palladium(II)		K_2CO_3	DMF	Air	90 °C	6 h	82	25
9	$\left[Pd\{C_6H_2(CH_2CH_2NH_2)-(OMe)_2,3,4\}Br(PPh_3) \right]$		K_2CO_3	NMP		130 °C	1 h	92	26
10	$\left[Pd(PhP(C_6H_4-2-S)_2)(PAr_3)\right]$		Cs_2CO_3	DMF		160 °C	4 h	85	27
11	Seven membered phosphine ylide palladacycle		K_2CO_3	NMP	Air	130 °C	24 h	90	28
12	PNP-SSS	—	K_2CO_3	Water		Reflux	5 h	92	29
13	Palladium dichloro-bis(aminophosphine) complexes	TBAB	K_2CO_3	NMP	N_2	100 °C	14 h	92	30
14	NHC-palladium complexes		K_2CO_3	NMP	Air	$105 \ ^{\circ}\mathrm{C}$	10 h	85	31
15	POM-IL-Pd		TEA	DMF		100 °C	2 h	49	32
16	$PdCl_2(DBPF)_2$	TBAC	Cy ₂ NMe	DMAc	_	80 °C	24 h	99	33
17	Pd ⁰ /SiO ₂		Na ₂ CO ₃	DMAc	Ar	135 °C			34
18	Pd(0)-MCM-41		NaOAc	DMF	_	100 °C	24 h	56	35
19	NHCs-Pd		KOAc	DMAc	_	140 °C	24 h	87	36
20	$Pd(OAc)_2$		K_3PO_4	DMAc	_	140 °C	25 h	98	37
21	PdCl ₂	GIL2	_	_	_	140 °C	1 h	96	38
22	Pd@MCOP	—	K ₂ CO ₃	DMSO-water (v/v)	—	90 °C	10 h	98	Present work

CB = cucurbituril; TPA = 12-tungstophosphoric acid; MIL = Materials of the Institute Lavoisier; SPIONs = superparamagnetic iron oxide nanoparticles; SSS = silica starch substrate; POM-IL = polyoxometalate-ionic liquid; DBPF = di-bisphosphenylferrocene; TBAB = tetrabutylammonium bromide; TBAC = tetrabutylammonium chloride; MCM = mesoporous silica matrix; GIL = guanidine based ionic liquids.

solid was isolated by filtration, washed with water, Pd@MCOP was obtained as brown powder, and kept under a nitrogen atmosphere.

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

Into a reaction tube equipped with a magnetic stirring bar were added 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). The mixture was stirred at 90 °C for a certain amount of 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 the organic layer was dried over anhydrous sodium sulfate. The organic solvent was evaporated under vacuum, the residues were purified by passing through a column of silica gel (60–120 mesh) affording the corresponding pure coupled product. The recovered catalyst was thoroughly washed with ethyl acetate and activated under vacuum at room temperature for 1 h, and subsequently reused.

Conclusions

In summary, we have developed a novel nitrogen rich functional mesoporous covalent organic polymer which functions as a good support for palladium nanoparticles (Pd@MCOP) as an heterogeneous catalyst with excellent catalytic activity in the 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, it is also environmentally friendly, highly stable, shows negligible metal leaching and can be reused under optimal conditions with only a minor loss of 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 industry.

Acknowledgements

PP gratefully acknowledges financial support from the University Grants Commission (UGC), New Delhi, for UGC-BSR-SRF. KP thanks DST, New Delhi for financial support.

References

 (a) A. P. Cote, A. I. Benin, N. W. Ockwig, A. J. Matzger, M. O'Keeffe and O. M. Yaghi, *Science*, 2005, **310**, 1166– 1170; (b) X. Feng, X. Dinga and D. Jiang, *Chem. Soc. Rev.*, 2012, **41**, 6010–6022; (c) J. F. Dienstmaier, D. D. Medina, M. Dogru, P. Knochel, T. Bein, W. M. Heckl and M. Lackinger, *ACS Nano*, 2012, **6**, 7234–7242; (d) S. Chandra, S. Kandambeth, B. P. Biswal, B. Lukose, S. M. Kunjir, M. Chaudhary, R. Babarao, T. Heine and R. Bannerjee, *J. Am. Chem. Soc.*, 2013, **135**, 17853–17861; (e) M. Dogru, M. Handloser, F. Auras, T. Kunz, D. Medina, A. Hartschuh, P. Knochel and T. Bein, Angew. Chem., Int. Ed., 2013, 52, 2920–2924.

- 2 (a) C. E. C. Thaw, A. Villa, P. Katekomol, D. Su, A. Thomas and L. Prati, Nano Lett., 2010, 10, 537-541; (b) Y. Yuan, H. Ren, F. Sun, X. Jing, K. Cai, X. Zhao, Y. Wang, Y. Wei and G. Zhu, J. Mater. Chem., 2012, 22, 24558-24562; (c) S. Kandambeth, A. Mallick, B. Lukose, M. V. Mane, T. Heine and R. Banerjee, J. Am. Chem. Soc., 2012, 134, 19524-19527; (d) H. A. Patel, S. H. Je, J. Park, D. P. Chen, Y. Jung, C. T. Yavuz and A. Coskun, Nat. Commun., 2013, 4, 1357; (e) S. Jin, K. Furukawa, M. Addicoat, L. Chen, T. Seiya, S. Irle, T. Nakamura and D. Jiang, Chem. Sci., 2013, 4, 4505-4511; (f) D. N. Bunck and W. R. Dichtel, Chem. Commun., 2013, 49, 2457-2459.
- 3 H. Deng, S. Grunder, K. E. Cordova, C. Valente, H. Furukawa, M. Hmadeh, F. Gandara, A. C. Whalley, Z. Liu, S. Asahina, H. Kazumori, M. O'Keeffe, O. Terasaki, J. F. Stoddart and O. M. Yaghi, *Science*, 2012, 336, 1018–1023.
- 4 (a) Y. Zhu, H. Long and W. Zhang, Chem. Mater., 2013, 25, 1630–1635; (b) H. Zhao, Z. Jin, H. Su, J. Zhang, X. Yao, H. Zhao and G. Zhu, Chem. Commun., 2013, 49, 2780–2782; (c) H. Zhao, Z. Jin, H. Su, X. Jing, F. Sun and G. Zhu, Chem. Commun., 2011, 47, 6389–6391; (d) X. Feng, L. Liu, Y. Honsho, A. Saeki, S. Seki, S. Irle, Y. Dong, A. Nagai and D. Jiang, Angew. Chem., Int. Ed., 2012, 51, 2618–2622; (e) S. Wan, J. Guo, J. Kim, H. Ihee and D. Jiang, Angew. Chem., Int. Ed., 2008, 47, 8826–8830; (f) S. Wan, F. Gandara, A. Asano, H. Furukawa, A. Saeki, S. K. Dey, L. Liao, M. W. Ambrogio, Y. Y. Botros, X. Duan, S. Seki, J. F. Stoddart and O. M. Yaghi, Chem. Mater., 2011, 23, 4094–4097; (g) Y. Zhang and S. N. Riduan, Chem. Soc. Rev., 2012, 41, 2083–2094.
- 5 (a) M. K. Bhunia, S. K. Das, P. Pachfule, R. Banerjee and A. Bhaumik, *Dalton Trans.*, 2012, 41, 1304–1311;
 (b) P. Puthiaraj and K. Pitchumani, *Chem. – Eur. J.*, 2014, 20, 8761–8770.
- 6 (a) P. Pachfule, S. Kandambeth, D. D. Diaz and R. Banerjee, Chem. Commun., 2014, 50, 3169–3172; (b) M. X. Tan, L. Gu, N. Li, J. Y. Ying and Y. Zhang, Green Chem., 2013, 15, 1127– 1132; (c) A. Modak, J. Mondal and A. Bhaumik, Chem-CatChem, 2013, 5, 1749–1753; (d) H. Li, B. Xu, X. Liu, S. A. C. He, H. Xia and Y. Mu, J. Mater. Chem. A, 2013, 1, 14108–14114; (e) S.-Y. Dimg, J. Gao, Q. Wang, Y. Zhang, W.-G. Song, C.-Y. Su and W. Wang, J. Am. Chem. Soc., 2011, 133, 19816–19822.
- 7 (a) J. Long, H. Liu, S. Wu, S. Liao and Y. Li, ACS Catal., 2013, 3, 647–654; (b) S. B. Kalidindi, H. Oh, M. Hirscher, D. Esken, C. Wiktor, S. Turner, G. V. Tendeloo and R. A. Fischer, Chem. Eur. J., 2012, 18, 10848–10856.
- 8 (a) E. Negishi, Handbook of Organopalladium Chemistry for Organic Synthesis, Wiley, Chichester, UK, 2002; (b) J. Tsuji, Palladium Reagents and Catalysts, Wiley, Chichester, UK, 2004; (c) T. Mizoroki, K. Mori and A. Ozaki, Bull. Chem. Soc. Jpn., 1971, 44, 581; (d) R. F. Heck and J. P. Nolley, J. Org. Chem., 1972, 37, 2320–2322; (e) A. F. Littke and

G. C. Fu, Angew. Chem., Int. Ed., 2002, **41**, 4176–4211; (f) I. J. S. Fairlamb, Tetrahedron, 2005, **61**, 9647–9655; (g) K. C. Nicolaou, P. G. Bulger and D. Sarlah, Angew. Chem., Int. Ed., 2005, **44**, 4442–4489.

- 9 (a) J. Magano and J. R. Dunetz, Chem. Rev., 2011, 111, 2177-2250; (b) V. F. Slagt, A. H. M. deVries, J. G. deVries and R. M. Kellogg, Org. Process Res. Dev., 2010, 14, 30-47; (c) C. Torborg and M. Beller, Adv. Synth. Catal., 2009, 351, 3027-3043; (d) H.-U. Blaser, A. Indolese, F. Naud, U. Nettekoven and A. Schnyder, Adv. Synth. Catal., 2004, 346, 1583-1598.
- 10 (a) A. F. Littke and G. C. Fu, J. Am. Chem. Soc., 2001, 123, 6989–7000; (b) K. H. Shaughnessy, P. Kim and J. F. Hartwig, J. Am. Chem. Soc., 1999, 121, 2123–2132; (c) T. E. Barder, S. D. Walker, J. R. Martineli and S. L. Buchwald, J. Am. Chem. Soc., 2005, 127, 4685–4696.
- 11 (a) G. Xie, P. Chellan, J. Mao, K. Chibale and G. S. Smith, Adv. Synth. Catal., 2010, 352, 1641-1647; (b) M. Amini, M. Bagherzadeh, Z. M. Shoeili and D. M. Baghaei, RSC Adv., 2012, 2, 12091-12095; (c) H. Hagiwara, Y. Sugawara, T. Hoshi and T. Suzuki, Chem. Commun., 2005, 23, 2942-2944; (d) S.-M. Lu and H. Alper, J. Am. Chem. Soc., 2005, 127, 14776-14784; (e) H.-J. Xu, Y.-Q. Zhao and X.-F. Zhou, J. Org. Chem., 2011, 76, 8036-8041; (f) N. T. S. Phan, M. V. Sluys and C. W. Jones, Adv. Synth. Catal., 2006, 348, 609-679; (g) G. P. McGlacken and I. J. S. Fairlamb, Eur. J. Org. Chem., 2009, 4011-4029; (h) D. Das, G. K. Rao and A. K. Singh, Organometallics, 2009, 28, 6054-6058; (i) F.-X. Felpin, K. Miqueu, J.-M. Sotropoulos, E. Fouquet, O. Ibarguren and J. Laudien, Chem. - Eur. J., 2010, 16, 5191-5204; (j) T. Chakraborty, K. Srivastava, H. B. Singh and R. J. Butcher, J. Organomet. Chem., 2011, 696, 2559-2564; (k) X. Zhou, J. Luo, J. Liu, S. Peng and G.-J. Deng, Org. Lett., 2011, 13, 1432-1435; (l) D.-H. Lee, A. Taher, S. Hossain and M.-J. Jin, Org. Lett., 2011, 13, 5540-5543; (m) B. Schmidt and N. Elizarov, Chem. Commun., 2012, 48, 4350-4352; (n) Y. Cai, G. Song and X. Zhou, Chin. J. Chem., 2012, 30, 2819-2822; (o) X. Wu, Y. Lu, H. Hirao and J. S. Zhou, Chem. - Eur. J., 2013, 19, 6014-6020
- (a) Y. Huang, S. Gao, T. Liu, J. Lu, X. Lin, H. Li and R. Cao, ChemPlusChem, 2012, 77, 106–112; (b) C. Evangelisti, N. Panziera, P. Pertici, G. Vitulli, P. Salvadori, C. Battocchio and G. Polzonetti, J. Catal., 2009, 262, 287–293; (c) M. A. Gotthardt, A. Beilmann, R. Schoch, J. Engelke and W. Kleist, RSC Adv., 2013, 3, 10676–10679; (d) A. Modak, J. Mondal, M. Sasidharan and A. Bhaumik, Green Chem., 2011, 13, 1317–1331; (e) D. Dey, T. Bhattacharya, B. Majumdar, S. Mandani, B. Sharma and T. K. Sarma, Dalton Trans., 2013, 42, 13821–13825; (f) M. Cao, Y. Wei, S. Gao and R. Cao, Catal. Sci. Technol., 2012, 2, 156–163.
- 13 K. Kanagaraj and K. Pitchumani, *Chem. Eur. J.*, 2013, **19**, 14425–14431.
- 14 C. Evangelisti, N. Panziera, A. D'Alessio, L. Bertinetti, M. Botavina and G. Vitulli, *J. Catal.*, 2010, **272**, 246–252.

- (a) A. Kamal, V. Srinivasulu, B. N. Seshadri, N. Markandeya, A. Alarifi and N. Shankaraiah, *Green Chem.*, 2012, 14, 2513– 2522; (b) S. Proch, Y. Mei, J. R. Villanueva, Y. Lu, A. Karpov, M. Ballauff and R. Kempe, *Adv. Synth. Catal.*, 2008, 350, 493–500; (c) S. Mukhopadhyay, G. Rothenberg, A. Joshi, M. Baidossi and Y. Sasson, *Adv. Synth. Catal.*, 2002, 344, 348–354; (d) Y. Wan, H. Wang, Q. Zhao, M. Klingstedt, O. Terasaki and D. Zhao, *J. Am. Chem. Soc.*, 2009, 131, 4541–4550; (e) H. Li, B. Xu, X. Liu, A. Sigen, C. He, H. Xia and Y. Mu, *J. Mater. Chem., A*, 2013, 1, 14108–14114.
- 16 (a) F. Zhang, J. Yin, W. Chai and H. Li, *ChemSusChem*, 2010, 3, 724–727; (b) J. Huang, J. Yin, W. Chai, C. Liang, J. Shen and F. Zhang, *New J. Chem.*, 2012, 36, 1378–1384.
- 17 (a) E. L. Spitler, J. W. Colson, F. J. U. Romo, A. R. Woll, M. R. Giovino, A. Saldivar and W. R. Dichtel, *Angew. Chem.*, *Int. Ed.*, 2012, 51, 2623–2627; (b) Z. Peng, Z. Shi and M. Liu, *Chem. Commun.*, 2005, 2125–2126.
- 18 A. C. Thomas, in *Photoelectron and Auger Spectroscopy*, Plenum, New York, 1975, p. 352.
- 19 W. J. Gammon, O. Kraft, A. C. Reilly and B. C. Holloway, *Carbon*, 2003, **41**, 1917–1923.
- 20 V. P. W. Bohm and W. A. Herrmann, *Chem. Eur. J.*, 2001, 7, 4191–4197.
- 21 S. Pathan and A. Patel, RSC Adv., 2012, 2, 116–120.
- 22 G. Ren, X. Cui, E. Yang, F. Yang and Y. Wu, *Tetrahedron*, 2010, **66**, 4022-4028.
- 23 H. Li, J. Lu, J. Lin, Y. Huang, M. Cao and R. Cao, Chem. Eur. J., 2013, 19, 15661–15668.
- 24 K. Khler, R. G. Heidenreich, J. G. E. Krauter and J. Pietsch, *Chem. Eur. J.*, 2002, **8**, 622–630.

- 25 M. Ghotbinejad, A. R. Khosropour, I. M. Baltork, M. Moghadam, S. Tangestaninejad and V. Mirkhani, *J. Mol. Catal. A: Chem.*, 2014, 385, 78–84.
- 26 A. R. Hajipour, F. Rafiee and A. E. Rouho, *Tetrahedron Lett.*, 2011, **52**, 4782–4787.
- 27 V. G. Benitez, S. H. Ortega, R. A. Toscano and D. M. Morales, *Inorg. Chim. Acta*, 2007, 360, 2128–2136.
- 28 S. J. Sabounchei, M. Ahmadi, M. Panahimehr, F. A. Bagherjeri and Z. Nasri, *J. Mol. Catal. A: Chem.*, 2014, 383–384, 249–259A.
- 29 K. Nezhad and F. Panahi, Green Chem., 2011, 13, 2408-2415.
- 30 M. Oberholzera and C. M. Frech, Green Chem., 2013, 15, 1678–1686.
- 31 J. Liu, Y. Zhao, Y. Zhou, L. Li, T. Y. Zhang and H. Zhang, Org. Biomol. Chem., 2003, 1, 3227–3231.
- 32 A. Corma, S. Iborra, F. X. L. Xamena, R. Monton, J. J. Calvino and C. Prestipino, *J. Phys. Chem. C*, 2010, 114, 8828–8836.
- 33 P. M. Murray, J. F. Bower, D. K. Cox, E. K. Galbraith, J. S. Parker and J. B. Sweeney, *Org. Process Res. Dev.*, 2013, 17, 397–405.
- 34 L. Huang, P. K. Wong, J. Tan, T. P. Ang and Z. Wang, J. Phys. Chem. C, 2009, 113, 10120–10130.
- 35 S. Jana, B. Dutta, R. Bera and S. Koner, *Inorg. Chem.*, 2008, 47, 5512–5520.
- 36 Q. Yao, M. Zabawa, J. Woo and C. Zheng, J. Am. Chem. Soc., 2007, 129, 3088–3089.
- 37 Q. Yao, E. P. Kinney and Z. Yang, J. Org. Chem., 2003, 68, 7528-7531.
- 38 S. Li, Y. Lin, H. Xie, S. Zhang and J. Xu, *Org. Lett.*, 2006, 8, 391–394.