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Nitrogen-rich porous covalent imine network (CIN) material as an efficient catalytic support for C–C coupling reactions[†]

Manas K. Bhunia,^a Swapan K. Das,^a Pradip Pachfule,^b Rahul Banerjee^b and Asim Bhaumik^{*a}

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In an effort to expand the realm of possibilities of nitrogen-rich porous materials that could be used in catalysis, herein we report the synthesis of a new highly nitrogen rich (*ca.* 45%) porous covalent imine network (CIN-1) material employing simple Schiff base chemistry and further grafting its surface with palladium. Pd-loaded CIN-1 support acts as a truly heterogeneous catalyst towards Suzuki C–C coupling reaction between aryl halides with arylboronic acids. High surface area and excellent accessibility of the catalytic sites make it very efficient for heterogeneous catalysis. The stability of the catalyst due to intimate contact between nitrogen-rich organic support and metal allows several reuses with only a minor loss in catalytic activity.

1. Introduction

Designing chemical reactions that will facilitate the creation of pores of desired dimensions is a challenging task to researchers. Such a goal might be achieved via covalent organic frameworks (COFs) because COFs are porous crystalline materials with pre-designed 2D and 3D polymer structures formed by covalently linked functionalities.¹⁻⁷ Synthesis of microporous organic polymers with a rational design at the molecular level using cheap and simple processes remains highly desirable. The newly developed nanoporous organic polymers, e.g., polymers of intrinsic microporosity (PIMs)⁸ and conjugated microporous polymers (CMPs),9 are new candidates for efficient and robust heterogeneous catalysts¹⁰ constructed through the "bottom-up" approach. Cooper and co-workers have shown that the pore size and surface area of nanoporous polymers may be finely tuned for versatile catalytic reactions by varying the molecular length of the building blocks.11 Introduction of multifaceted functionality12-15 into porous networks is one of the frontline areas of research, which could lead to the development of new materials with diverse applications. Incorporation of an active functionality, for example nitrogen groups, on the surface of the supported materials may be beneficial to enhance the catalytic performance as well as the stability of the supported materials. Jiang et al. have demonstrated that the introduction of nitrogen functionalities on the surface of carbon nanotubes¹⁶ (CNTs) increases the dispersion and the stability of gold nanoparticles. The strong interaction of gold nanoparticles with the nitrogen-doped carbon nanotubes is mainly responsible for homogeneous distribution of the gold nanoparticles. Nitrogen-doped CNTs used for supporting metal nanoparticles show better activity than pristine CNTs, when used as catalyst for the Heck reaction of iodobenzene and styrene¹⁷ Palladium-loaded nitrogen-doped CNTs can act as a catalyst for hydrogenation of cinnamaldehyde into hydrocinnamaldehyde.¹⁸ More recently, Thomas *et al.*¹⁹ have shown that the nitrogen-rich covalent triazine framework can act as a catalytic support for liquid-phase glycerol oxidation. Indeed immobilized metal sites in heterogeneous molecular catalysts based on polymeric porous materials possessing ligand motifs within the material structure are very reactive.²⁰ Imines are of fundamental importance in synthetic chemistry, and the basic reaction mechanism for their formation from an aldehyde and an amine is described elsewhere.^{21,22}

Herein, melamine and 1,4-piparazinedicarbaldehyde have been chosen for the Schiff-base condensation reaction, as we envisioned that this reaction would lead to the incorporation of piparazine units on edges and melamine at vertices (Scheme 1) and thus make certain the uniform arrangement of both nitrogen-rich components in the network. Significant amounts of nitrogen have been incorporated into comparable inorganic framework materials²²⁻²⁵ and this is found to be beneficial for the storage of gases and the stabilization of metal species. We found that the reaction led to formation of the desired porous structure having highest nitrogen content (*ca.* 45%) among other such type of microporous networks.²⁵

During the last few decades, the mild and selective Suzuki coupling reaction involving nucleophilic arylboronic acids with aryl halides^{26,27} has almost completely replaced classical methods for the synthesis of biaryl compounds and has become highly useful in designing target pharmaceuticals and fine chemicals.²⁸⁻³⁰ The biaryl substructure occurs quite frequently in biologically active components and functional molecules. More than 7000

^aDepartment of Materials Science, Indian Association for the Cultivation of Science, Jadavpur, Kolkata, 700 032, India. E-mail: msab@iacs.res.in ^bPhysical and Materials Chemistry Division, National Chemical Laboratory, Pune, 411 008, India

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Scheme 1 Schematic representation of the porous covalent imine network (CIN-1).

publications³¹ demonstrate the tremendous research interest in improving this transformation. In the last few years, a number of ligand-free heterogeneous Pd catalysts on various supports have emerged^{32,33} offering easy catalyst recovery. These ligand-free heterogeneous systems face some drawbacks including the need to use surfactants in aqueous solution^{34,35} or microwave radiation³⁶ to assist phase transfer. Despite the improved conversion and yield, such additives also lead to problems, such as product contamination, more laborious downstream purification, and increased cost. Thus the design and synthesis of highly porous supports, along with the control over the interaction between support and metal, is the key parameter in designing highly active catalysts and is a stimulating challenge.

We have developed different functionalized mesoporous silicas with imine functionality at the surface and grafted these materials with palladium to form supported catalysts for different C-C coupling reactions.^{37,38} Palladium nanoparticle systems have lower catalytic activity than that of the homogeneous counterpart and palladium atoms often leach irreversibly from the support, limiting long-lived recyclable use.³⁹⁻⁴¹ Thus, the long-term stability via palladium grafting along with reusability are clear goals. In this context, nitrogen-rich covalent organic frameworks may offer a large number of metal binding sites and improved thermal stability. Herein, we first report a new microporous network material CIN-1 through interlinking of strong covalent imine bonds, its Pd-grafting and subsequently its high catalytic performance in Suzuki C-C coupling reaction. The porous support materials have been prepared through simple Schiff-base reaction of relatively cheap, industrially important and readily accessible chemicals, without using any surfactant as structure directing agent.

2.1. Chemicals

Melamine and 1,4-piparazine dicarbaldehyde were purchased from Sigma-Aldrich. All other reagents and chemicals were purchased from commercial sources and were used without further purification. Solvents were dried and distilled through standard procedure.

2.2. Synthesis of covalent imine network (CIN) materials

A round-bottom flask fitted with a condenser and a magnetic bar was charged with piparazine dicarbaldehyde (169 mg, 1.19 mmol) and melamine (100 mg, 0.79 mmol) and dimethyl sulfoxide (12 mL). The flask was degassed by dry nitrogen and refluxed at 453 K for 72 h in the inert atmosphere. After cooling to room temperature the precipitated off-white product was isolated by filtration over a Büchner funnel and washed with dry ethanol and excess dry acetone, THF and dichloromethane sequentially. Finally, the product was dried in vacuum to obtain the desired solvent-free powder (257 mg, 95.5% yield). All the washing solvents were dried and distilled following standard procedure.

2.3. Preparation of catalyst

A mixture of $Pd(OAc)_2$ (10 mg, 0.044 mmol) in acetone (20 mL) and CIN-1 material (250 mg) was stirred at room temperature (298–300 K) for 48 h. When a yellow solid appeared, it was then filtered through G4 sintered glass crucible and washed with acetone (4 × 5 mL) to remove any trace amount of un-reacted Pd(OAc)₂. It was then dried in the oven at 353 K overnight to provide an easy flowing pale yellow powder. This CIN-supported Pd catalyst (Pd-CIN-1, Pd content = 0.60 wt%, determined by AAS) was used for all the Suzuki coupling reactions.

3. Characterization techniques

FT-IR spectra were obtained on a Nicolet MAGNA-IR 750 spectrometer with samples prepared as KBr pellets. Elemental analysis was carried out in a 2400 Series-II CHN Analyzer, Perkin-Elmer, USA. The ${}^{13}C{}^{1}H{}$ cross-polarization magic-angle spinning (CP-MAS) NMR spectrum was obtained on a Bruker DSX 500 at 125.8 MHz and a MAS frequency of 25 kHz. The ¹³C cross-polarization was performed using a contact time of 3 and 7 ms, respectively, and a high-power ¹H decoupling two-pulse, phase modulation (TPPM) of 100 kHz. The ¹³C NMR spectra were referenced with respect to tetramethylsilane using adamantine (13C, 29.456 ppm) as secondary standard. Nitrogen adsorption-desorption isotherms were obtained using a Quantachrome Autosorb 1 C surface area analyzer at 77 K. Prior to gas adsorption, all the samples were degassed for 4 h at 453 K. Transmission electron microscopic images and selected area electron diffraction (SAED) patterns were recorded on a JEOL 2010 TEM operated at 200 kV. A JEOL JEM 6700 field emission scanning electron microscope (FE-SEM) was used for the determination of morphology of the particles. Atomic absorption spectroscopy (AAS) analysis was carried out using palladium standards on a Shimadzu AA-6300 atomic absorption spectrophotometer. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of samples were carried out in a TGA instruments thermal analyzer TA-SDT Q-600 under N₂ flow. ¹H NMR spectra were recorded on a Bruker 300 MHz spectrometer. The chemical shifts (δ) are reported in parts per million, using TMS as an internal standard and CDCl₃ as the solvent. In catalytic reaction product conversion was monitored by gas chromatography (GC). At selected time intervals the products were collected from the reaction mixture and analyzed by capillary gas chromatography (Agilent 4890D, FID).

3.1. Catalytic conditions

In a typical reaction a mixture of phenylboronic acid (145 mg, 1.2 mmol), 4-bromobenzaldehyde (185 mg, 1 mmol), Pd loaded CIN-1 catalyst (5 mg of solid catalyst), and K₂CO₃ (1.2 mmol, 170 mg) in DMF (2 mL) was heated at 353 K for 0.5–3.5 h. The progress of the reaction was monitored by TLC. The reaction mixture was extracted with dry Et₂O (3×10 mL), and the ether extract was washed with brine solution and water and dried over Na₂SO₄. Then evaporation of solvent left the crude product which was purified by column chromatography over silica gel [R_f 0.85 (hexane–ether 9:1)] to give biphenyl-4-carbaldehyde as a white solid (178 mg, 98%). The spectroscopic data (IR, ¹H NMR and ¹³C NMR) are in good agreement with the reported values. This is the general method that carried out for all other substrates for Suzuki C–C coupling reactions by using Pd-CIN-1 catalyst.

3.2. Leaching test

The Suzuki C–C cross coupling reaction was carried out in dimethyl formamide (DMF) solvent. After the completion of a given reaction the product was filtered off and washed with acetone and then the filtrate was evaporated to dryness. An appropriate amount of nitric acid (30 wt%) was added to the filtrate, and the resulting sample adjusted to 5 wt% nitric acid was applied to characterize the Pd leaching. Pd content in the filtrate was estimated by using a Shimadzu AA-6300 atomic absorption spectrophotometer. Atomic absorption spectrometric analysis of the liquid phase revealed the absence of any detectable palladium in the filtrate solution.

3.3. Hot filtration test

The Pd-CIN-1 catalyst (5 mg), K_2CO_3 (1.2 mmol, 170 mg) in DMF (2 mL) and a mixture of phenyl boronic acid (145 mg, 1.2 mmol), 4-bromobenzaldehyde (185 mg, 1 mmol) were heated at 353 K. The Pd-CIN-1 catalyst was filtered off (from the hot reaction mixture) after 15 min. when 57% conversion was achieved (GC and ¹H NMR) and the reaction was continued with the filtrate for another 1 h. Absolutely no increase in the amount of product was observed beyond 57%. It is further noted that palladium is also not detected (AAS) in the liquid phase after the completion of the reaction for 1 h and that the filtrate remains completely colorless.

3.4. Three-phase test

Amino-functionalized 2D-hexagonal mesoporous silica material was prepared through co-condensation of tetraethyl orthosilicate (TEOS) and 3-aminopropyltriethoxysilane (APTES) in the presence of pluronic P123 ($M_{av} = 5800$, EO₂₀PO₇₀EO₂₀), tri-

block copolymer as structure directing agent in acidic aqueous medium and its organic templates removed through acidic ethanol solution extraction. The desired amount of amino-functionalized silica (AFS) was then refluxed with *p*-bromoacetophenone in dry ethanol in nitrogen atmosphere for 2 h. It was then cooled to room temperature and filtered and repeatedly washed with ethanol to remove unreacted *p*-bromoacetophenone, and dried to obtain the PBA-MS material. A three-phase test was performed to confirm whether the reactions are truly heterogeneous catalysis or not. A mixture of phenylboronic acid (145 mg, 1.2 mmol), 4bromobenzene (156 mg, 1 mmol), Pd loaded CIN-1 catalyst (5 mg of solid catalyst), 1 g PBA-MS, and K₂CO₃ (1.2 mmol, 170 mg) in DMF (2 mL) was heated at 353 K for 1.5 h. It was then cooled to room temperature, extracted with water and ether and then washed with brine solution, and dried over Na₂SO₄. The extracted product was analyzed by GC and ¹H NMR which showed ca. 96% of 4-bromobenzene was converted to biphenyl. The obtained residue was refluxed with 2 M HCl and the solution was extracted and analyzed by GC and ¹H NMR.

3.5. Recycle test

After the completion of the Suzuki coupling reaction on a given aryl bromide (4-bromobenzaldehyde), the Pd-CIN-1 catalyst was recovered by centrifugation, and then washed thoroughly with DMF followed by copious amounts of water to remove the base present in the used catalyst, and finally by acetone to remove the unreacted boronic acid. The recovered catalyst was dried under vacuum at 353 K overnight and activated at 373 K for 2 h. This used catalyst was re-employed in next cycle under identical conditions. Similarly another three successive cycles have been performed. In every cycle at selected time intervals the products were collected from the reaction mixtures and analyzed by capillary gas chromatography (Agilent 4890D,FID) and ¹H NMR (Bruker 300 MHz spectrometer).

4. Results and discussion

An imine-functionalized highly nitrogen-rich porous covalent organic network has been synthesized by Schiff base condensation reaction of rigid triamine and relatively flexible dialdehyde. The as-prepared sample was thoroughly washed with dry acetone and other volatile solvents to remove dimethyl sulfoxide. The synthesized materials were thoroughly characterized by means of IR and ¹³C CP-MAS NMR spectroscopy, transmission and scanning electron microscopy, elemental microanalysis, powder XRD and nitrogen gas adsorption studies.

The FT IR spectrum of CIN-1 (Fig. 1) shows imine (C==N) stretches at 1635 and 1198 cm⁻¹ clearly confirming the imine bond formation. The nodal lines resulting from standing waves are used to identify the quadrant and semicircle vibrations of heteroaromatic ring systems. The distinct bands related to the quadrant (1550 cm⁻¹) and semicircle stretching (1480 cm⁻¹) of the triazine ring are present in the spectrum of the CIN-1 material, indicating the successful incorporation of melamine into the network. There was no peak at 2877 cm⁻¹ and at around 1653 cm⁻¹ confirming the absence of any unreacted aldehyde in the asprepared sample (Fig. S1, ESI†). Detailed assignments of the FT IR peaks are given in ESI†.



Fig. 1 Infrared transmittance spectra of (a) melamine, (b) 1,4-piparazine dicarbaldehyde and (c) as-prepared CIN-1 materials. Arrows correspond to peaks at 1635, 1550, 1480, 1198 cm⁻¹. Full assignment of the peaks is given in ESI[†].

The ¹³C cross-polarization magic-angle spinning (CP-MAS) NMR spectral study was performed to confirm the chemical structure of the sample (Fig. 2). The NMR signal at 53.53 ppm originates from the CH₂ aliphatic carbons of the piparazine ring. A significantly more intense peak at 166.07 ppm is indicative of the triazine rings as well as the imine functionality. Small peaks centred at 33.56 and 13.44 can be attributed to the methyl carbon of DMSO solvent and methylene carbon of ethanol solvent that are used in the synthesis procedure. Whereas the melamine rings are rigid, the prepared porous network of CIN-1 is flexible, due to the presence of non-aromatic piparazine rings.



Fig. 2 ¹³C CP/MAS NMR spectrum for CIN-1. Full assignment of the peaks is given in ESI[†].

A field emission scanning electron microscopic (FE SEM) image of the as-synthesized CIN-1 depicts spherical-like nanoparticles of size *ca*. 50–60 nm (Fig. 3). Particles with nanoscale dimensions are particularly demanding from the catalysis point of view to overcome diffusional limitations. CHN elemental analysis revealed *ca*. 41.6 wt% nitrogen content, whereas SEM-EDS results suggested *ca*. 48% N in CIN-1. These values are in close agreement with theoretical N-content of 44.2 wt%, indicating a highly



Fig. 3 SEM image of the as-prepared porous polymer depicting nanoparticles of spherical-like morphology.



Fig. 4 Transmission electron microscopic images of (a) as-prepared CIN-1 and (b) palladium loaded-CIN-1 (inset shows a palladium nanoparticle).

nitrogen-rich porous polymer network in CIN-1. HR TEM images (Fig. 4) suggested the existence of high electron density spherical spots of dimension *ca.* 8–10 nm throughout the specimen, which are assigned to Pd-nanoparticles in Pd-CIN-1. Nevertheless, like other microporous polymers based on cross-linking or Schiff base chemistry,²⁵ CIN-1 is mostly amorphous (Fig. S3a, ESI†). TGA results suggested *ca.* 20 wt% loss up to 593 K along with moderately high thermal stability of CIN-1 (Fig. S4, ESI†).

 N_2 sorption analysis of CIN-1 (Fig. 5) showed a steep gas uptake at low relative pressures ($P/P_0 = 10.82-12.42 \times 10^{-4}$)



Fig. 5 Nitrogen adsorption–desorption isotherm of (a) as-prepared CIN-1 and (b) palladium-loaded-CIN-1.



Fig. 6 Plots of pore size distributions of (a) as-prepared CIN-1 and (b) palladium-loaded-CIN-1.

thus reflecting the microporous nature of the polymer networks. Further, it showed gradual rise in the intermediate P/P_0 suggesting mesoporosity in the material, which could be attributed to inter-nanoparticle voids. Pore size distribution (PSD) of the as-synthesized CIN-1 material estimated by non-local density functional theory (NLDFT) assuming slit/cylindrical pores using an equilibrium model is shown in Fig. 6. This PSD pattern suggested a peak pore diameter of 1.0 nm for CIN-1. After the loading of Pd into the porous CIN-1 material the pore diameter decreases to <1 nm. Very consistent pore size (ca. 0.83 nm) distribution has been obtained by using the H-K method⁴² which is specifically applicable to estimate pore diameters of <1.0 nm. The BET equivalent surface area and pore volume of CIN-1 were 580 m² g⁻¹ and 0.33 cm³ g⁻¹, respectively, whereas for Pdloaded material Pd-CIN-1 these values decreased to 163 m² g⁻¹ and 0.18 cm³ g⁻¹, respectively (Table 1, multipoint BET plots shown in Fig. S5, ESI[†]). The Langmuir surface areas of CIN-1 and Pd-CIN-1 are 623 and 177 m²g⁻¹, respectively. Thus, the surface areas as well as pore volumes are considerably reduced on Pd loading. This could be attributed to the dispersion of Pd on the surface of the porous network and some sort of pore blocking can also occur. Pd loading in Pd-CIN-1 was ca. 0.60 wt% (estimated by AAS). The very small hysteresis in the sorption profile of CIN-1 compared to that in Pd-CIN-1, suggested adsorption and desorption are equally facile in the former, whereas bottle-neck type pores are formed on Pd loading in this covalent imine network.

As the prepared CIN-1 material has large amount of nitrogen from triazine and imine functionalities together with high surface

Table 1	Physico-	-chemical	properties	of porous	CIN-1	and Pd-CIN-	1
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Sample	Surface area/ $m^2 g^{-1}$	Pore width/nm	Pore volume/cm ³ g ⁻¹
CIN-1	580	1.0–1.96/4.18	0.33
Pd-CIN-1	163	0.83–1.1	0.18

area it could be an excellent metal species stabilizer. We stirred CIN-1 with a Pd(OAc)₂ solution in acetone at room temperature for 48 h to obtain the Pd-CIN-1 catalyst. The TEM image analysis of the catalyst (shown in Fig. 4b) suggested the presence of palladium nanoparticles (8–10 nm in diameter). It is instructive to suggest that the imine functionalities along with triazine nitrogen may act as the reducing agent as well as stabilizer in the formation of supported palladium nanoparticles.⁴³

The catalytic activity of Pd-loaded imine-functionalized material Pd-CIN-1 was tested for the liquid-phase Suzuki C-C cross coupling reaction over various electron-withdrawing and electrondonating aryl halides. A range of substituted aryl bromides were used as substrates. The entries in Table 2 revealed that for both electron withdrawing and electron donating groups very high yields of the respective biaryl derivatives are formed. Compared with electron-donating substituents, the electron withdrawing groups exhibited a positive effect on the reaction and resulted in a facilitated coupling process, reaching a moderately high turnover number (TON; moles of substrate converted per moles of Pd, assuming all palladium atoms are present at the surface of the Pd-nanoparticles and that each participates in the catalysis) value in a relatively short reaction time. Turnover numbers (TONs) was calculated on the basis of moles of Pd present in the supported catalyst (5 mg) as estimated by atomic absorption spectroscopy. The moderate turnover numbers are attributed to the relatively high catalyst loading. Presumably, longer reaction times combined with either lower catalyst loadings (lower molar ratios) result in higher TONs.44,45 We used different halide substituted aryl bromides as substrates, and intriguingly the Pd-CIN-1 showed high chemoselectivity for halogen substituted aryl bromides in the

 Table 2
 Suzuki coupling with bromoarenes catalyzed by palladiumanchored CIN-1 catalyst^a

R^1	\rightarrow Br + $\boxed{\frac{1}{2}}$ R ²	∕-в(с	DH) ₂	Pd-CIN-1 Cat DMF, K ₂ CO ₃ 353 K	$\begin{array}{c} t \\ \hline \\ R^1 \end{array}$	$- \left\langle \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$
Entry	\mathbf{R}^{1}	\mathbb{R}^2	t/h	Yield ^b (%)	TON ^c	TOF ^d
1	4-Me	Н	2.5	96	1470	588
2	4-OMe	Н	3.5	97	1500	429
3	2-CHO	Н	1.0	97	1485	1485
4	4-CHO	Н	1.0	98	1500	1500
5	2-COMe	Н	1.0	95	1454	1454
6	4-CN	Н	0.5	96	1470	2940
7	$4-CF_3$	Н	1.0	95	1454	1454
8	Н	Н	1.5	96	1470	980
9	4-NO ₂	Н	0.5	94	1439	2878
10	4-F	Н	1.0	92	1408	1408
11	4-Cl	Н	1.5	96	1470	980

^{*a*} Bromoarene (1 mmol), arylboronic acid (1.2 mmol), Pd-CIN-1 cat. (0.01 mol%) and K₂CO₃ (1.2 mmol) were stirred at 353 K for the required period of time in 2 mL DMF solvent. ^{*b*} Yleids refer to those of purified products characterized by spectroscopic data. ^{*c*} TON (Turnover number) = moles converted/moles of active sites. ^{*d*} TOF = TON/time.

C-C coupling reaction. To demonstrate this, we employed fluoride and chloride substituted phenyl bromide as reacting substrates, resulting in the fluoro- and chloro-substituted biaryl products in good yields clearly showing the reaction pathway occuring only through bromo-intermediates.

Heterogeneous Pd loaded catalysts are advantageous compared to homogeneous catalysts because of easy product isolation, catalyst recovery and reusability while palladium immobilization induces a dramatic increase in catalytic activity of heterogeneous catalysts as compared to homogeneous versions.46-48 Different reported heterogeneous catalysts⁴⁹⁻⁵¹ however present various limitations such as low surface area of the supports, which decreases the adsorption of the reactants, the dispersion of metallic sites and their accessibility. Furthermore, poor stability of these catalysts and metal leaching constitute major drawbacks, both for selectivity and recycling of the catalyst.⁵²⁻⁵⁴ In our system the enhanced catalytic activity could be due to the high surface area of the CIN-1, which provides better dispersion of the Pd nanoparticles (Fig. 4) and thus excellent accessibility of the surface-bound catalytic sites.⁴¹ Moreover, strong metal interaction with the multiple nitrogens of the triazine and imine functionalities present in the network provides excellent stability of the supports, as well as preventing metal leaching during the course of the reaction.

To investigate the heterogeneous nature of the catalysis taking place in our system and to refute any possibility of homogeneous catalysis due to the leaching of the palladium into the solution, we performed a hot filtration test by using 4-bromobenzaldehyde as standard substrate. The hot filtration test consists the stopping of the reaction at half-conversion and filtering of the catalyst without cooling the solution so as to circumvent redeposition of the palladium particles in the supported material. In our system the reaction was stopped after 15 min (57% conversion) and then quickly the catalyst was separated by sintered glass crucible. After the filtration process, the filtrate was immediately reused for the same reaction in an identical reaction condition, but no further conversion was observed (GC/¹H NMR), that proved the absence of any active species in the filtrate solution. Again, when the reaction was carried out in the absence of catalyst, almost no conversion was found.

A three-phase test was performed to confirm whether the reactions are truly heterogeneous. For that amino-functionalized mesoporous silica (AFS) has been taken and reacted with pbromoacetophenone to obtain PBA-MS (Fig. 7). A mixture of phenylboronic acid (145 mg, 1.2 mmol), 4-bromobenzene (156 mg, 1 mmol), Pd loaded CIN-1 catalyst (5 mg of solid catalyst), 1 g PBA-MS and K₂CO₃ (1.2 mmol, 170 mg) in DMF (2 mL) was heated at 353 K for 1.5 h. The reaction flask was cooled to room temperature and after that the product was extracted with water and diethyl ether. The organic part was washed with minimum water (three times) and then separated and washed with brine solution, and dried over Na₂SO₄. The extracted product was analyzed by GC and ¹H NMR which showed ca. 96% of 4bromobenzene converted to biphenyl. The obtained residue was refluxed with 2 M HCl and the solution was extracted and analyzed by GC and ¹H NMR. The product was *p*-bromoacetophenone which makes us convinced that anchored *p*-bromoacetophenone in mesoporous silica did not take part in the C-C coupling reaction and remained intact in the silica matrix. If any palladium leached



Fig. 7 (a) Amino-functionalized mesoporous silica preparation and (b) anchoring of p-bromoacetophenone on amino-functionalized silica matrix.

to the solution, then anchored *p*-bromoacetophenone would take part in the coupling reaction. Nonetheless this did not occur with Pd-CIN-1 presented here. Thus, this three-phase test provides further evidence that the reaction is truly heterogeneous in nature and there is no leaching of palladium during the course of reaction.

Furthermore, we have studied the recyclability of Pd-CIN-1 in the model Suzuki cross-coupling reaction using 4bromobenzaldehyde as substrate. Kinetic investigations for the first run revealed that the coupling reaction was completed within 1 h (Fig. 8). The catalyst was separated from the reaction mixture by centrifugation and was thoroughly washed with ample amounts of dimethyl formamide, water and acetone to remove the unreacted reactants, and then dried in an oven at 353 K overnight and then activated at 373 K for 2 h. Then the recovered catalyst was reused in the next round of coupling reactions. Owing to the built-in nature of the covalently linked imine network with catalytic sites, Pd-CIN-1 maintains its structure well and allows for a robust recycling capability, with well-retained activity up to five cycles.



Fig. 8 Kinetic plots of recycling test of catalyst (Pd-CIN-1) in the Suzuki coupling reaction with 4-bromobenzaldehyde as substrate.

The percentage of conversions vs. time for the consecutive runs is shown in Fig. 8. From the kinetic plot it has been observed that efficiency of the catalyst decreases quite slowly. This slow deactivation of the Pd-CIN-1 catalyst can be explained by the enhanced stability of metal support due to strong interaction between Pd and the functionalities in the network. Chan-Thaw et al.¹⁹ observed the same behavior when they introduced nitrogen functionalities on the surface of Pd/CTF supported material. To get an insight on the deactivation process, we have also examined the state of the catalysts by TEM analysis. TEM images of the catalyst after the first run show almost similar distribution of palladium particles as for the as-prepared catalyst, nevertheless, very slight metallic aggregation has been observed (Fig. 9). Powder XRD experiment of the catalyst after the first run has been performed to investigate the crystallinity of the nanoparticles (Fig. S6a, ESI[†]). The diffraction patterns show retained crystallinity as for the as-synthesized catalyst with peaks at 40.0, 46.7, 68.3 and 82.2° which can be assigned to the (111), (200), and (220) planes of face-centered cubic (fcc) structure of Pd having Fm3m space group.55 The peak intensity is, however, considerably reduced compared to that of the powder pattern of the as-prepared catalyst (Fig. S3, ESI[†]). This can be attributed to the some extent of disordering occurring during the course of the catalytic reaction.



Fig. 9 TEM images of the recycled catalyst after the first run.

Suzuki coupling of bromobenzene with phenylboronic acid under heterogeneous conditions over a variety of catalysts has been studied in recent years (Table 3). Sayari and co-workers⁵⁶ have developed the Pd/PE-MCM-41 catalyst which shows 61% conversion within 20 h in Suzuki coupling of bromobenzene with phenylboronic acid. Copper oxide support with high loading (7.0%) of oval shape Pd(0) materials only give 80% conversion within 10 h.40 Very recently, Quignard et al.57 have also performed the same Suzuki coupling reaction in the presence of Ca, Pd/alginate catalyst that gives 95% conversion within 5 h. Our newly synthesized palladium loaded covalent imine network material efficiently confers 96% conversion within only 1.5 h for the same coupling reaction. Owing to the strong covalent imine bonds and high nitrogen content (ca. 45%) the CIN-1 networks provide good dispersion and strong interaction of the palladium results as an efficient catalyst for Suzuki coupling. It is noteworthy to mention here that we have succeeded to improve the catalytic efficiency of the Pd-loaded catalyst for Suzuki coupling with respect to time, temperature and yield compared to the reported results (Table 3).40,56,57

 Table 3
 Suzuki coupling of bromobenzene with phenylboronic acid catalyzed by a variety of catalysts

Entry	Catalyst (Pd, mol%)	t/h	Base	T/K	Yield (wt%)	Ref.
1	Pd/PE-MCM-41 (0.1)	20	$\begin{array}{c} K_3PO_4\\ K_2CO_3\\ K_2CO_3\\ K_2CO_3\end{array}$	295	61.0	55
2	CuO/Pd-3 (7.0)	10		353	80.0	40
3	Ca, Pd/alginate (0.4)	5.0		343	95.4	56
4	Pd-CIN-1 (0.6)	1.5		353	96.0	This work

5. Conclusion

We can conclude that a facile synthesis of imine-functionalized nitrogen-rich porous organic network can be developed from relatively cheap and industrially important building blocks by employing an easy chemical route. With the view of possible catalytic application, palladium has been loaded on its surface and the resulting material showed excellent catalytic activity towards Suzuki carbon–carbon cross coupling reaction in the absence of any additional stabilizing ligand over a very short reaction time. The high amount of nitrogen in the CIN-1 support makes the Pd nanoparticles resistant to aggregation and also helps to preserve their catalytic activity and stability during recycling. Thus, our functional covalent porous material paves the new strategy towards the development of organic network materials having extensive catalytic applications.

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References

- (a) A. P. Côté, A. I. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger and O. M. Yaghi, *Science*, 2005, **310**, 1166–1170; (b) C. J. Doonan, D. J. Tranchemontagne, T. G. Glover, J. R. Hunt and O. M. Yaghi, *Nat. Chem.*, 2010, **2**, 235–238.
- 2 P. Kuhn, M. Antonietti and A. Thomas, *Angew. Chem., Int. Ed.*, 2008, **47**, 3450–3453.
- 3 R. W. Tilford, S. J. Mugavero, P. J. Pellechia and J. J. Lavigne, Adv. Mater., 2008, 20, 2741–2746.
- 4 M. Rose, W. Böhlmann, M. Saboa and S. Kaskel, *Chem. Commun.*, 2008, 2462–2464.
- 5 F. J. Uribe-Romo, J. R. Hunt, H. Furukawa, C. Klock, M. O'Keeffe and O. M. Yaghi, J. Am. Chem. Soc., 2009, 131, 7216–7217.
- 6 A. L. Korich and P. M. Iovine, Dalton Trans., 2010, 39, 1423-1431.
- 7 O. K. Farha, Y-S. Bae, B. G. Hauser, A. M. Spokoyny, R. Q. Snurr, C. A. Mirkin and J. T. Hupp, *Chem. Commun.*, 2010, **46**, 1056–1058.
- 8 N. B. McKeown and P. M. Budd, Chem. Soc. Rev., 2006, 35, 675
- 9 J. X. Jiang, F. Su, A. Trewin, C. D. Wood, N. L. Campbell, H. Niu, C. Dickinson, A. Y. Ganin, M. J. Rosseinsky, Y. Z. Khimyak and A. I. Cooper, *Angew. Chem.*, *Int. Ed.*, 2007, 46, 8574.
- 10 X. Du, Y. Sun, B. Tan, Q. Teng, X. Yao, C. Suc and W. Wang, *Chem. Commun.*, 2010, 46, 970–972.
- 11 J. X. Jiang, F. Su, A. Trewin, C. D. Wood, H. Niu, J. T. A. Jones, Y. Z. Khimyak and A. I. Cooper, J. Am. Chem. Soc., 2008, 130, 7710.
- 12 L. Wang, A. Reis, A. Seifert, T. Philippi, S. Ernst, M. Jia and W. R. Thiel, *Dalton Trans.*, 2009, 3315–3320.
- 13 S. Singha, M. Sahoo and K. M. Parida, *Dalton Trans.*, 2011, 40, 7130– 7132.
- 14 D. Chandra, B. K. Jena, C. R. Raj and A. Bhaumik, *Chem. Mater.*, 2007, **19**, 6290–6296.
- 15 S. K. Das, M. K. Bhunia, A. K. Sinha and A. Bhaumik, ACS Catal., 2011, 1, 493–501.

- 16 K. Jiang, A. Eitan, L. S. Schadler, P. M. Ajayan and R. W. Siegel, *Nano Lett.*, 2003, 3, 275.
- 17 H. Yoon, S. Ko and J. Jang, Chem. Commun., 2007, 1468.
- 18 J. Amadou, K. Chirazi, M. Houllé, I. Janowska, O. Ersen, D. Bégin and C. Pham Huu, *Catal. Today*, 2008, **138**, 62.
- 19 C. E. Chan-Thaw, A. Villa, P. Katekomol, D. Su, A. Thomas and L. Prati, *Nano Lett.*, 2010, **10**, 537–541.
- 20 C. W. Jones, Top. Catal., 2010, 53, 942-952.
- 21 E. H. Cordes and W. P. Jencks, J. Am. Chem. Soc., 1962, 84, 832.
- 22 P. Pandey, A. P. Katsoulidis, I. Eryazici, Y. Wu, M. G. Kanatzidis and
- S. T. Nguyen, *Chem. Mater.*, 2010, 22, 4974–4979.
 23 J. Germain, F. Svec and J. M. J. Fréchet, *Chem. Mater.*, 2008, 20, 7069–7076
- 24 P. Kuhn, A. Thomas and M. Antonietti, *Macromolecules*, 2009, 42, 319–326.
- 25 M. G. Schwab, B. Fassbender, H. W. Spiess, A. Thomas, X. Feng and K. Müllen, J. Am. Chem. Soc., 2009, 131, 7216–7217.
- 26 N. Miyaura and A. Suzuki, Chem. Rev., 1995, 95, 2457.
- 27 J. Hassan, M. Sevignon, C. Gozzi, E. Schulz and M. Lemaire, *Chem. Rev.*, 2002, **102**, 1359.
- 28 L. J. Gooßen, G. Deng and L. M. Levy, Science, 2006, 313, 662.
- 29 L. Yin and J. Liebscher, Chem. Rev., 2007, 107, 133-173.
- 30 R. Dey, B. Sreedhar and B. C. Ranu, *Tetrahedron*, 2010, **66**, 2301–2305.
- 31 SciFinder topic search through CAS for "Suzuki coupling" resulted in 7270 hits to date.
- 32 H. Sakurai, T. Tsukuda and T. Hirao, J. Org. Chem., 2002, 67, 2721–2722.
- 33 V. Polshettiwar, C. Len, A. Fihri and Coord, *Chem. Rev.*, 2009, **253**, 2599–2626.
- 34 E. Paetzold and G. Oehme, J. Mol. Catal. A: Chem., 2000, 152, 69-76.
- 35 S. Bhattacharya, A. Srivastava and S. Sengupta, *Tetrahedron Lett.*, 2005, 46, 3557–3560.
- 36 S. S. Yi, D. H. Lee, E. Sin and Y. S. Lee, *Tetrahedron Lett.*, 2007, **48**, 6771–6775.

- 37 (a) K. Sarkar, M. Nandi, M. Islam, M. Mubarak and A. Bhaumik, *Appl. Catal.*, *A*, 2009, **352**, 81–86; (b) K. Dhara, K. Sarkar, D. Srimani, S. K. Saha, P. Chattopadhyay and A. Bhaumik, *Dalton Trans.*, 2010, **39**, 6395–6402.
- 38 A. Modak, J. Mondal, V. K. Aswal and A. Bhaumik, J. Mater. Chem., 2010, 20, 8099–8106.
- 39 M. Choi, D.-H. Lee, K. Na, B.-W. Yu and R. Ryoo, Angew. Chem., Int. Ed., 2009, 48, 3673.
- 40 K. Chattopadhyay, R. Dey and B. C. Ranu, *Tetrahedron Lett.*, 2009, 50, 3164–3167.
- 41 S. Ogasawara and S. Kato, J. Am. Chem. Soc., 2010, 132, 4608-4613.
- 42 G. Horvath and K. Kawazoe, J. Chem. Eng. Jpn., 1983, 16, 470–475. 43 I. P. Beletskaya and A. V. Cheprakov, Chem. Rev., 2000, 100, 3009–
- 3066.
 44 K. Shimizu, T. Ka-no, T. Kodama, H. Hagiwara and Y. Kitayama, *Tetrahedron Lett.*, 2002, 43, 5653–5655.
- 45 A. Corma, H. Garcia, A. Leyva and A. Primo, *Appl. Catal., A*, 2004, **257**, 77–83.
- 46 T. Vincent and E. Guibal, Langmuir, 2003, 19, 8475.
- 47 R. Narayanan and M. A. El-Sayed, J. Catal., 2005, 234, 348-355.
- 48 J. M. Richardson and C. W. Jones, J. Catal., 2007, 251, 80–93.
- 49 F. X. L. Xamena, A. Abad, A. Corma and H. Garcia, J. Catal., 2007, 250, 294–298.
- 50 R. B. Bedford, C. S. J. Cazin, M. B. Hursthouse, M. E. Light, K. J. Pike and S. Wimperis, *J. Organomet. Chem.*, 2001, **633**, 173–181.
- 51 C.-H. Lu and F.-C. Chang, ACS Catal., 2011, 481-488.
- 52 K. Yu, W. Sommer, M. Weck and C. W. Jones, J. Catal., 2004, 226, 101–110.
- 53 A. Behr, G. Henze and R. Schomaecker, Adv. Synth. Catal., 2006, 348, 1485–1495.
- 54 S. Kozuch and J. M. L. Martin, ACS Catal., 2011, 1, 246-253.
- 55 J. Liu, F. He, E. Durham, D. Zhao and C. B. Roberts, *Langmuir*, 2008, **24**, 328.
- 56 D. D. Das and A. Sayari, J. Catal., 2007, 246, 60-65.
- 57 A. Primo, M. Liebel and F. Quignard, Chem. Mater., 2009, 21, 621-627.