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Pd NPs decorated over hypercrosslinked microporous polymer: a highly efficient catalyst for the formylation of amines via carbon dioxide fixation reaction

Rostam Ali Molla,[a] Piyali Bhanja,[b] Kajari Ghosh,[a,c] Sk Safikul Islam,[a,d] Asim Bhaumik,*[b] Sk Manirul Islam*[a]

Abstract: CO_2 fixation reaction is one of the most challenging chemical transformations not only in the context of environmental remediation but for effective utilization of abundant carbon sources of nature. Here, we have stabilized palladium nanoparticles (NPs) at the surfaces of a hypercrosslinked porous polymer bearing carbazole and α,α'-dibromo-*p*-xylene monomeric units to obtain Pd@HMP-1 nanocatalyst. The material has been thoroughly characterized by powder XRD, HR TEM, FE-SEM, BET, TGA and FTIR analysis. Pd@HMP-1 showed excellent catalytic activity towards formylation of amines via carbon dioxide fixation reaction under mild reaction conditions. High surface area and nitrogen rich porous surface make the polymer suitable support for the palladium nanoparticles and its high recycling efficiency in this CO_2 fixation reaction.

1. Introduction

The carbon dioxide fixation reactions and its transformation to the value added chemicals are very demanding in the context of greenhouse gas control[1] and cost-effectiveness and green organic synthesis as CO_2 is a nontoxic, cheap and abundant renewable C1 source.[2] Substitution of hazardous and toxic carbon monoxide as a C1 source with carbon dioxide, is a greener and sustainable move towards the production of carbonyl group containing various important chemicals.[3] Up till now a wide range of methodologies have been developed for the carbon dioxide fixation reactions such as carboxylation of aryl halides/alkynes,[4,5] formylation of aryl halides,[6,7] formylation of amines,[8-10] methylation of amines and cyclization with epoxides or aziridines.[11-15] Formylation of amines using carbon dioxide as the C1 source is a very useful reaction as most of the N-formylated products are used as the intermediates of various agrochemicals, fragrances, drugs and dyes.[16-20] There are two pathways to produce formylated amines, one is non carbon dioxide pathway and the second one is carbon dioxide fixation pathway. In case of non CO_2 pathway either formaldehyde or methanol is used as a CHO source.[21-23] On the other hand, carbon dioxide fixation pathway involving CO_2 as C-source is more attractive than non CO_2 pathway in terms of economy and environmental concerns.

First homogeneous catalytic system for N-formylation has been reported by Haynes et al. using CO_2 and H_2 for the production of DMF[24] followed by Noyori and co-workers using ruthenium based homogeneous catalyst.[25,26] Recently, synthesis of formamides from amines *via* CO_2 fixation reaction using hydrosilane or molecular hydrogen as the hydrogen source has been reported. However, utilization of H_2 as a reducing agent required harsh reaction conditions[27] compared to hydrosilanes.

In last few years, the utilization of hydrosilanes as reducing agent of carbon dioxide has increased tremendously.[28-30] Cantat et al have used the hydrosilane for the formylation of amines via CO_2 fixation reaction.[31-32] Latter on some other catalytic systems such as imidazolium-based ionic liquids[33] and thiazolium carbine[34] were reported. The former catalytic system showed good recyclability. Non recyclable and homogeneous metal salts based catalysts make the separation process difficult and costly. To avoid the separation difficulties and also to make process cost effective Gao et *al*. have reported covalent organic frameworks as heterogeneous catalyst for this CO_2 fixation reaction in the presence of immobilized ionic liquids.[35] On the other hand, high surface area, excellent stability of the polymeric framework and tunable functional groups at the pore surface has made the porous organic polymers a very demanding material for a wide range of frontline applications. Recently, hypercrosslinked porous organic polymers have been used as a solid support for noble metal nanoparticles.[36-39] The synergy of the porous organic polymer bearing metal binding sites and nanoparticles offer exceptional recyclability and high activity in several catalytic reactions.

Herein, we report the synthesis of a hypercrosslinked microporous polymer via Friedel-Crafts alkylation reaction between α,α'-dibromo-*p*-xylene and carbazole. The resulting hypercrosslinked microporous polymer HMP-1 is used as support to stabilize tiny palladium nanoparticles to obtain Pd@HMP-1. The Pd@HMP-1 material showed excellent catalytic activity for the carbon dioxide fixation reaction with amines under mild reaction conditions. The excellent stability, recyclability and efficiency of the catalyst could be attributed due to the strong binding of reactive Pd NPs on nitrogen containing hypercrosslinked microporous structure.

2. Experimental

Synthesis of hypercrosslinked microporous polycarbazole supported palladium nanomaterial (Pd@HMP-1):

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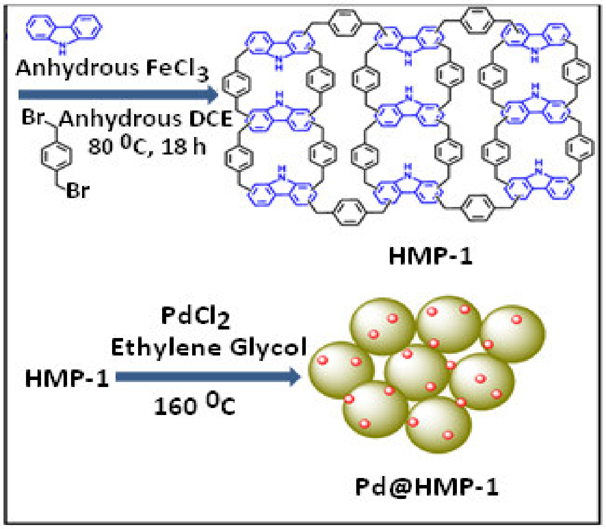
Supporting information for this article is given via a link at the end of the document. ((Please delete this text if not appropriate))

For synthesizing microporous polycarbazole based organic framework we have explored the Friedel-Crafts alkylation reaction.[40] α,α'-dibromo-p-xylene and carbazole undergoes the Friedel-Crafts alkylation reaction in the presence of $FeCl_3$ catalyst. In a typical reaction 50 mmol of α,α'-dibromo-p-xylene (13.2 gm) and 25 mmol of carbazole (4.15 gm) and 8.5 gm $FeCl_3$ were mixed in anhydrous dichloroethane (DCE) and stirred for 6 h under N_2 atmosphere at room temperature. After that the temperature of the reaction mixture was increased to 80 ^{0}C and refluxed for 18 h. A brown colored precipitate was obtained and to remove iron completely the precipitate was washed with methanol by soxhlet apparatus. Again it was washed with acetone and hexane consecutively and then dried in vacuum for overnight to obtain HMP-1.

500 mg HMP-1 was taken in a round bottomed flask and 60 mg $PdCl_2$ and 10 ml distilled water was added to it and stirred for 1h at 100 ^{0}C. After that temperature was increased for complete evaporation of water. It was then cooled to room temperature followed by addition of 10 ml ethylene glycol and then stirring for 5 h at 160 ^{0}C. Finally the product was washed with methanol and dried (Scheme 1) to obtain Pd@HMP=1.



Scheme 1: Schematic synthesis procedure polycarbazole supported Pd NPs (Pd@HMP-1)

General procedure of formylation of amine:

Formylation of amines was carried out in a 50 ml stainless-steel reactor outfitted with a temperature controller and stirrer. 1.0 mmol of amine, 2.0 mmol of dimethylphenylsilane, 5 ml dioxane, and 60 mg catalyst (Pd@HMP-1) were added in the high-pressure reactor and then reactor was pressurized with CO_2 (1 MPa) at 60 ^{0}C for 9h and then 0.3 ml of distilled water injected in the reactor and continued for total 20 h. After completion of reaction, the reactor was cooled, the CO_2 was vented from the reactor and the product was analyzed by GC.

3. Results and Discussion

3.1. Characterizations

The loading of palladium in Pd@HMP-1 has been estimated through the AAS analysis and the observed palladium loading in the catalyst was 4.52 weight %. We have carried out CHN analysis to investigate the carbon, hydrogen and nitrogen content in Pd@HMP-1, where observed C = 80.43 %, H = 5.72 % and N = 4.26 %. Theoretically the carbon, hydrogen and nitrogen content have been estimated to be 89.54 %, 5.86 %, 4.60 %, respectively. Close N contents in Pd@HMP-1 with respect to the proposed model structure of Scheme 1 with stoichiometric ratio of the monomers suggested full incorporation of carbazol moieties in the crosslinked polymeric backbone.

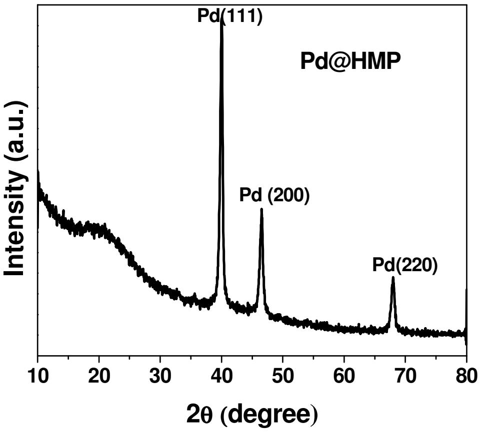


Figure. 1 XRD analysis of Pd@HMP-1 material

Powder X-ray diffraction pattern of Pd@HMP-1 material is shown in Figure 1. Microporous HMP-1 showed its distinguishing wide diffraction hump located at 2θ=19-21 degree which suggested the amorphous nature of the polymeric material. High surface area of the material is capable to bind the nanoparticles at its surface with the help of nitrogen donor sites. Accordingly, Pd@HMP-1 material showed three additional prominent diffraction peaks at 40.20, 46.35 and 68.10 degrees corresponding to Pd(111), Pd(200) and Pd(220) FCC crystal planes of metallic palladium.[41]

Microscopic analysis

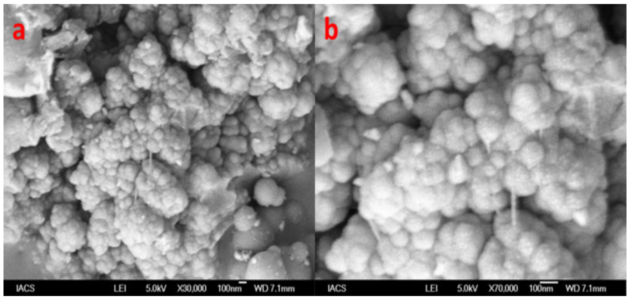


Figure 2. The FE-SEM images of Pd@HMP-1 material at two different magnifications

In order to understand the morphological features of Pd@HMP-1, field emission scanning electron microscopic (FE-SEM) image analysis has been carried out. In Figures 2a and 2b the SEM images of Pd@HMP-1 material are shown at two different magnifications. It is noticed from Figure 2b the Pd@HMP-1 particles have spherical particle morphology with dimensions of *ca.* 80-90 nm. These spherical particles are agglomerated to form larger particles and this could be responsible for inter-particle porosity as seen from the BET analysis.

Specific surface area, porosity:

The nitrogen adsorption/desorption isotherm of Pd@HMP-1 material is shown in Figure 3. As seen from the figure that the isotherm can be classified as mixture of type I and IV according to IUPAC nomenclature.[42,43] Initially the gradual N_2 uptake at 0 to 0.1 partial pressure P/P_0 region suggests the presence of micropores in the material. This is followed by gradual increase in N_2 uptake in the partial pressure P/P_0 region 0.20 to 0.90

suggested the presence of mesopores. These mesopores could be attributed to the inter-particle porosity in the nanoscale. BET

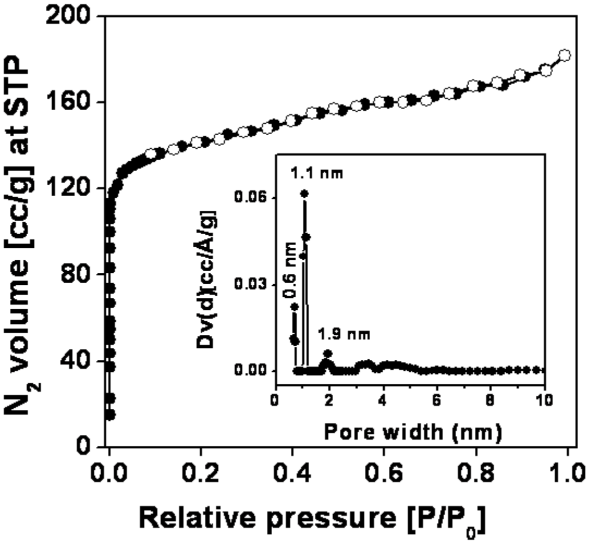


Figure 3. The N_2 adsorption/desorption isotherm of Pd@HMP-1 material where filled circle represents adsorption and empty circle defines desorption. The pore size distributions plot, obtained by using NLDFT (Non Local Density Functional Theory) method, is shown in the inset.

(Brunauer, Emmett and Teller) surface area and the pore volume were 384 m^{2}g^{-1} and 0.2171 ccg^{-1}, respectively. Utilizing NLDFT (non-local density functional theory) method the pore size distribution plot has been demonstrated in the inset of Figure 3 where the peak pore diameters for Pd@HMP-1 of 0.6, 1.1 and 1.9 nm is observed. Peak pore diameter of parent HMP-1 as observed at 1.6 nm[40] has been reduced to 1.1 nm after Pd loading in Pd@HMP-1. From De Boer statistical thickness (*t*-plot) the microporosity and mesoporosity contribution to the total BET surface area of material are calculated as 338 and 46 m^{2}g^{-1}, respectively.

HR TEM analysis:

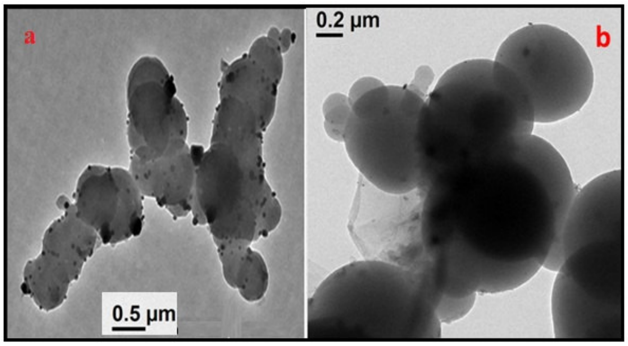


Figure 4 HR TEM images of Pd@HMP-1 material.

In Figure 4, high resolution TEM images of the Pd@HMP-1 material are shown. The TEM images provide a clear idea about the morphology of the Pd NPs in the material. Spherical nature polymeric material with interconnected morphology is seen in this TEM image (Fig. 4b). On the other hand, black dots at the surface of the round shaped polymer are due to the deposition of the palladium nanoparticles on the surface of the HMP-1 material. Figure 4b confirms the palladium nanoparticles with a diameter of ~10-15 nm has been grafted successfully over the polymer surface.

Thermal analysis

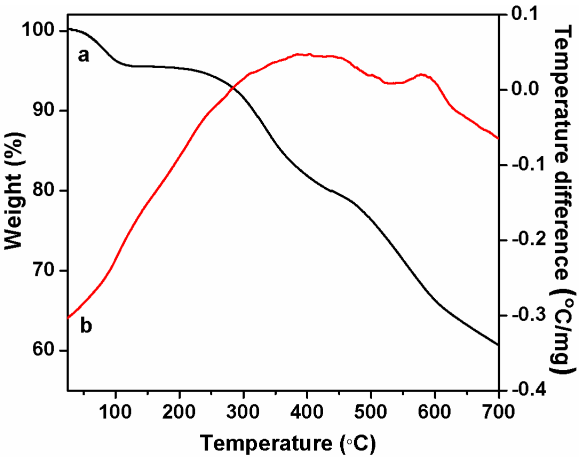


Figure 5. The TGA (a) and (b) DTA profile diagrams of Pd@HMP-1 material.

To check the thermal stability of Pd@HMP-1 material thermogravimetric analysis has been performed at 10 ^{0}C temperature ramp under N_2 flow up to 700 ℃. Figure 5 represents the TG/DTA profile diagram for Pd@HMP-1 material. The initial weight loss at ca. 90-120 ^{0}C could be attributed to the evaporation of adsorbed moisture from the material surface. Further, a second weight loss has been observed in the temperature region of 240 to 440 ℃ due to decomposition of organic functional groups of polymeric framework. The third weight loss started at 480 ℃ is for the decomposition of residual part of material. The thermal analysis data revealed the good thermal stability of Pd@HMP-1 material upto 240 ℃.

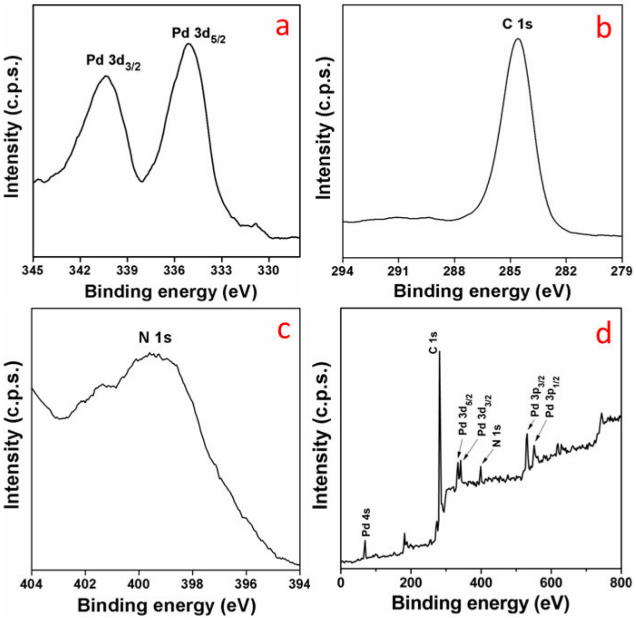
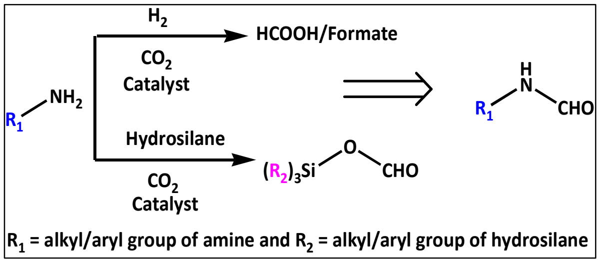


Figure 6. Narrow range XPS spectra of Pd@HMP-1 material containing elements Pd 3d (a), C 1s (b), N 1s (c), and full scale XPS survey spectrum (d).

To get a better idea about the oxidation state of metal centre as well as binding sites with organic part XPS analysis has been performed. Figure 6 represents the narrow range XPS spectrum of Pd@HMP-1 material, which suggested the presence of elements C 1s (a), N 1s (b), Pd 3d (c), and Pd 3p (d). Figure 6c shows the XPS spectrum of Pd 3d with two binding energy values at 334.8 eV and 340.5 eV, corresponding to two splitting component $3d_{5/2}$ and $3d_{3/2}$, respectively.[44] Further, since the material is devoid of O, two peaks in the binding energy range 530-570 eV corresponds to the Pd $3p_{3/2}$ and $3p_{1/2}$.This result suggested the presence of zero oxidation state of palladium (Pd^0) in Pd@HMP-1. The N 1s peak at 399.3 eV is attributed to the presence of carbazole moiety, which can coordinate with the Pd centres.

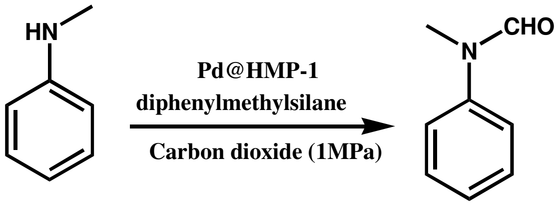
Catalytic Activity:

Recently we have synthesized few porous nanomaterials and utilized them in the carbon dioxide fixation reactions.[45,46] In this work we have synthesized palladium nanoparticles supported on nitrogen bearing crosslinked porous polymer and this catalyst has been explored in the formylation of amines using CO_2. Literature reports suggested that there are two ways to produce formylated amines *via* carbon dioxide fixation reaction. Molecular H_2 was used as reducing agent in one path and in another alternative pathway, where hydrosilane was used as the reducing agent using simple tetrabutylammonium fluoride or hydroxide as catalyst.[47]



Scheme 2: Formylation of amine through different pathways.

We have started the formylation reaction of the N-methylaniline with diphenylmethylsilane as the reducing agent of carbon dioxide. Initially we have taken 1 mmol of N-methylaniline, 2 mmol of diphenylmethylsilane and 5 ml of dioxane at 1 MPa CO_2 pressure. The outcome of the result was interesting and we have got 87 % of formylated product of N-methylaniline.



Scheme 3: Formylation of N-methylaniline catalyzed by Pd@HMP-1

For optimization we have screened all the parameters. Solvent is very important parameter for the reaction. Thus we have tested some other solvents like THF and toluene but these solvents were not superior to dioxane for the reaction. Similarly reducing agent is also important. We have employed hydrogen as a reducing agent but desired yield was low. Detailed study is given in the Table 1. To increase the desired yield we have injected 0.5 ml water after 6h (Table 1, entry 5). The increase in yield (%) can be explained on the basis of previous literatures which suggested that formic acid or formate salt formed in the reaction medium, reacted with amine to produce formylated amine.[48,49] Thus we have injected small amount of water in the reactor under the given reaction condition (Table 1, entry 5) which may produce formic acid and it can further react with N-methylaniline to generate N-phenylformamide.

Table 1: Effect of solvent and reducing agent on the N-formylation reaction.

Entry	Solvent	Reducing agent	GC yield (%)
1	Toluene	diphenylmethylsilane	15
2	THF	diphenylmethylsilane	58
3	Dioxane	diphenylmethylsilane	87
4	Dioxane	H_2 (1.5MPa)	23
5[a]	Dioxane/H_2O	diphenylmethylsilane	93

Reaction conditions: N-methylaniline (1.0 mmol), Dioxane (5 ml), CO_2 (1MPa), diphenylmethylsilane (2.5 mmol), Pd@HMP-1 (50 mg), Temperature (60 ^{0}C), time 20h. [a]Reaction condition: 0.3 ml water was added after 9h

The reaction parameters such temperature and catalyst amount are also important in terms of conversion and selectivity. Both the parameters are optimized (Table 2). We have tested the reaction even at low temperature (30 ^{0}C) and got moderately good yield. Conversion of the N-methylaniline increases with temperature, at 60 ^{0}C temperature maximum yield was obtained. Beyond this temperature selectivity of the N-methyl-N-phenylformamide started to decrease slightly and N, N-dimethylaniline was started to form. The amount of catalyst which was required to get maximum yield was optimized. When catalyst loading was low (20 mg) the amount of desired yield was also low (36 %). The highest yield of N-formylated product was obtained when catalyst amount was 50mg. Reaction time was also optimized and at 20 h maximum yield was obtained.

Table 2: Effect of catalyst amount and temperature on the N-formylation reaction

Entry	Catalyst amount (mg)	Temperature (^{0}C)	GC yield (%)
1	50	30	56
2	50	40	68
3	50	50	85
4	50	60	93
5	50	80	88
6	20	60	36
7	40	60	79
8	-	60	-
9[a]	50	60	90

Reaction conditions: N-methylaniline (1.0 mmol), diphenylmethylsilane (2.5 mmol), dioxane (5 ml + 0.3 ml water was added after 9h), CO_2 (1Mpa), time 20h. [a]Reaction time (15 h).

Effect of CO_2 pressure on the reaction was checked by varying pressure from 0.1 MPa to 1.2 MPa. When CO_2 pressure was low (near 1 atmosphere) yield of N-methyl-N-phenylformamide was below 20 %. But when CO_2 pressure was increased, yield was also increased. Maximum yield was formed at 1 MPa pressure, after that yield remained almost constant (Fig.7).

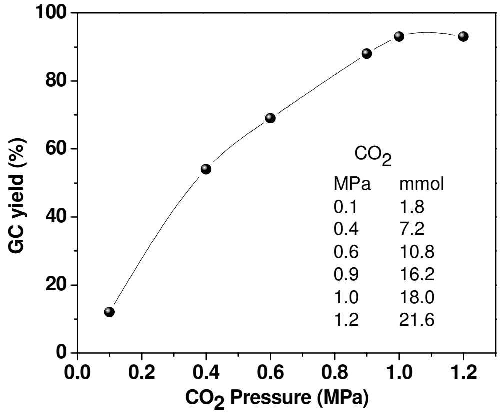


Figure 7. Effect of CO_2 pressure on the N-formylation reaction.

Reaction conditions: N-methylaniline (1.0 mmol), diphenylmethylsilane (2.5 mmol), Dioxane (5 ml + 0.3 ml water was added after 9h), time 20 h.

We have also tested the effect of some other supports on this N-formylation reaction (Table 3). We have loaded Pd NPs over the TiO_2 nanoparticles. When Pd/TiO_2 was employed as catalyst the selectivity of formylated yield was decreased due to the formation of N-methylated product (Table 3, product-B). Commercially purchased Pd/C was also active for the reaction but the yield (%) was low compared to Pd@HMP-1. In the absence of PdNPs, HMP-1 was also gave the desired the product (22%), which could be attributed due to the presence of N-donor siltes present at the HMP-1 surface. Only trace amount of the desired product was obtained in the absence of any catalyst (Table 3, entry 6). HMP-1 alone can also catalyze the reaction to a certain extent. Basic nitrogen sites are present inside the pore and as well as outside the pore *i.e* on the external surface. These basic nitrogens is also be able to promote the interation between amine and silane which facilitated the reaction to some extent and thus produced small amount desired N-formylated product.

Table 3. Effect of different catalysts on formylation of aniline

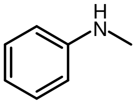
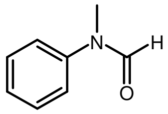
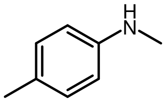
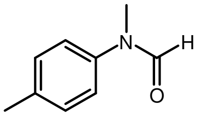
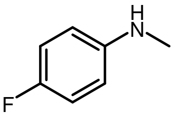
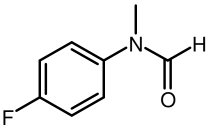
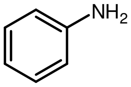
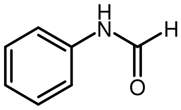
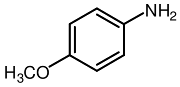
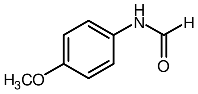
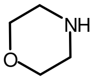
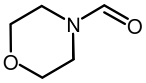
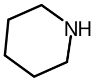
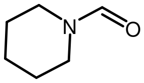
$$R\text{-}NH_2 \longrightarrow \underset{A}{RNHCHO} \longrightarrow \underset{B}{RNHCH_3}$$

Entry	Catalyst	A (%)	B (%)
1	Pd@TiO_2	58	36
2	Pd@C	84	-
4	HMP-1	22	-
5	Pd@HMP-1	93	-
6	without catalyst	0.4	-

Reaction conditions: aniline (1.0 mmol), diphenylmethylsilane (2.5 mmol), Dioxane (5 ml + 0.3 ml water was added after 9h), CO_2 (1MPa),temperature (60 ^{0}C), Catalyst (50 mg), time 20h.

Under the optimized reaction conditions we have tested some other amines such as substituted aniline, morpholine and piperidine. All the mentioned substrates (Table 4, entries 1-7) produced their corresponding formamide with excellent yield. Based on our experimental results and literature reports[50,51] we can propose a mechanistic pathway for the N-formylation reaction over Pd@HMP-1 and this is shown in Scheme 4. Main role of the support is immobilization of the active centres. Initially Si-H bond of Me_2PhSiH has been activated by palladium nanoparticle present in Pd@HMP-1 and consequently activated silane reacts with carbon dioxide to form formyloxysilane intermediate (i) which further reacts with amine to form desired product. On the other hand, intermediate (i) reacts with water to form HCOOH. Microporous polymer containing the free N-donor sites of carbazole can catalyze the reaction between formic acid and amine to produce N-fomylated product (Scheme 4).

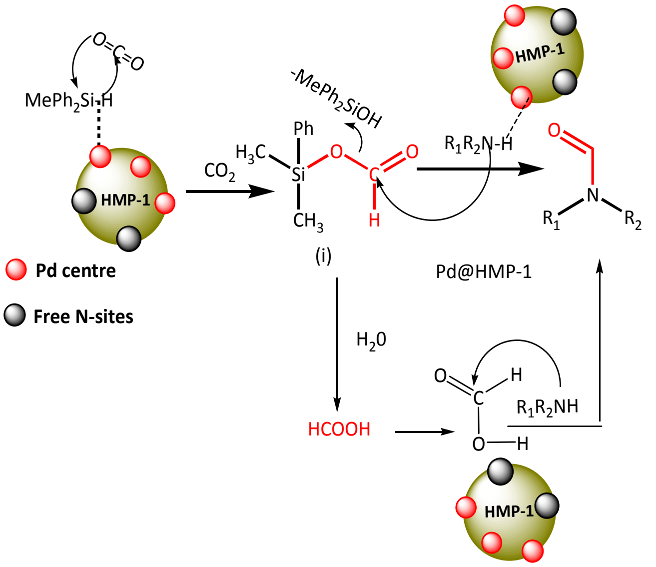
Table 4. Formylation of various amines under optimized reaction conditions

Entry	Substrate	Product	GC yield (%)
1			93
2			91
3			88
4			79
5			87
6			97
7			95

Reaction conditions: Amine (1.0 mmol), diphenylmethylsilane (2.5 mmol), Dioxane (5 ml + 0.3 ml water was added after 9h), CO_2 (1MPa),temperature (60 ^{0}C), Pd@HMP-1 (50 mg), amine: palladium molar ratio is 1:0.021, time 20h.

Catalyst reusability:

The Pd-HMP-1 catalyst showed very good recyclability in this N-formylation reaction. At the end of the reaction the catalyst was removed by plain filtration washing with acetone. The catalyst was dried up in oven at 80 ^{0}C. Under the optimized reaction condition the catalyst employed for 2nd run and it was observed that efficiency of the catalyst was lowered by only 2%. In this way the catalyst can be reused upto 5 times. In these successive cycles almost similar reactivity was observed (Fig. 8). This result suggested that Pd@HMP-1 is a very efficient catalyst for the N-formylation reaction. We have carried out the same recycling experiments with 10 mg catalyst instead of 50 mg catalyst. In that perticular case we have got 28% yield for the 1st cycle and 21% for the 5th reaction cycle. Little decrease in the product yield during the recycling experiment could be attributed to minor deactivation and loss of catalysts during the workup.



Scheme: 4: Probable reaction path way of N-formylation of amines.

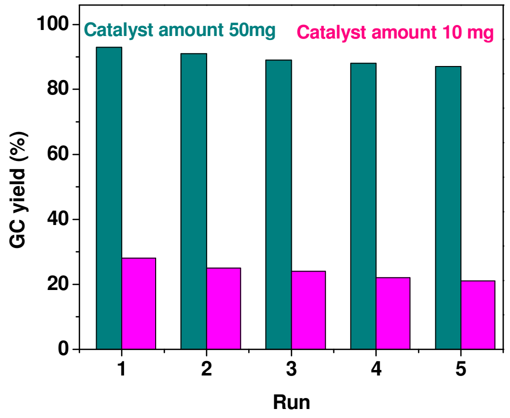


Figure 8 Recyclability test of the catalyst (Pd@HMP-1).

It is pertinent to mention that in the nitrogen containing porous polymer HMP-1, the nitrogen functionality may present inside the pore as well as outside the pore i.e on the internal and external surface of the material. So, it can bind a Pd metal either through inside the pore or outside surface depending upon the size of nanoparticle.[52] TEM images suggests that the size of the Pd NPs are mostly larger than pore size. Thus, nitrogen present at the external surface of the pores bind the nanoparticles firmly.

Table 3 entry 4 showed that the reaction may also carried out some extent in the presence of microporous HMP-1 polymer alone. But reactivity of the catalyst is much higher when Pd nanoparticles are loaded on HMP-1. So, the nitrogen present in the microporous material (HMP-1) can plays two important role; first is to stabilize the Pd nanoparticles on the porous surface (mainly through outer surface nitrogen) and secondly is helps to catalyze the reaction. Recently, Gao et al have reported the formylation reaction using microporous COF material ([Et$_4$NBr]50%-py-COF, pore size 1.6 nm).[53] Thus, this formylation can also be carried out within the micropores bearing the active sites. So, the main role of Pd@HMP-1 material with nitrogen containing micropores is to act as a supporting centre to enhance the overall productivity of the reaction.

Conclusion

In conclusion, palladium nanoparticles are supported efficiently over a hypercrosslinked microporous polycarbazole (Pd@HMP-1) and the resulting material can catalyze the formylation of amines in the presence of carbon dioxide as C1 source. In this reaction diphenylmethylsilane is used as effective reducing agent in the presence of CO$_2$. Various aromatic and non aromatic amines produced their corresponding formylated amines. The crosslinked polymer containing nitrogen sites can bind the palladium nanoparticle at the surface of the polymer very strongly. The catalyst can be recycled several times without much decrease in its activity. Thus, the protocol reported herein for the synthesis of Pd NPs decorated hypercrosslinked microporous polymer and its efficient use in the CO$_2$ fixation reaction under green conditions for the N-formylated products may open new avenues in environmental and catalysis research in near future.

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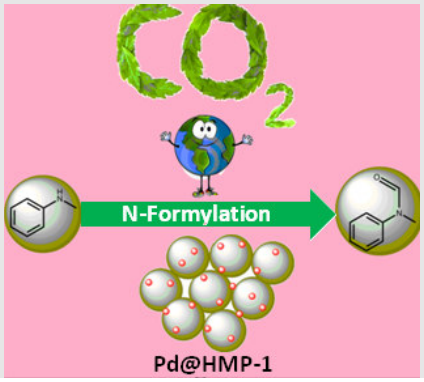

CO_2 fixation via formylation of amines: Pd nanoparticles are grafted at the surface of a hypercrosslinked porous polymer and the resulting material showed high catalytic activity towards formylation of a wide range of aromatic amines via carbon dioxide fixation reaction under mild conditions.

Rostam Ali Molla, Piyali Bhanja, Kajari Ghosh, Sk Safikul Islam, Asim Bhaumik,* Sk Manirul Islam*

Pd NPs decorated over hypercrosslinked microporous polymer: a highly efficient catalyst for the formylation of amines via carbon dioxide fixation reaction