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A Route for Direct Transformation of Aryl Halides to Benzyl Alcohols via Carbon Dioxide Fixation Reaction Catalyzed By (Pd@N-GMC) Palladium Nanoparticles Encapsulated Nitrogen Doped Mesoporous Carbon Material

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Abstract

A nitrogen doped mesoporous carbon material was synthesized from glucose and melamine under hydrothermal treatment. Soft template, brij-35 was used as a template. Nitrogen containing high surface area and porous channels make this material an important support for palladium nanoparticles as well as carbon dioxide capturing agent. Ethylene glycol was used as a reducing agent for the palladium nanoparticles synthesis. The palladium nanoparticles embedded porous nitrogen doped carbon material (Pd@N-GMC) was used for the synthesis of benzyl alcohols from aryl iodides via carbon dioxide fixation reaction. The catalyst was highly stable and reusable without any significance loss of its activity.

1. Introduction

In recent years, synthesis of value-added products from carbon dioxide (CO_2) has attracted much interest.[1] CO_2 is a more green and economical C1 source than carbon monoxide (CO) because CO_2 is non toxic, cheap, easy to handle, renewable and environmental friendly.[2] Activation of CO_2 and consequently CO_2 transformation of activated form of CO_2 to chemicals is highly challenging due to high stability of CO_2.[3] Up till now, several works have been reported on CO_2 involved chemical conversion. So far carbon dioxide was used for the synthesis of cyclic carbonate, aldehyde, carboxylic acid, alcohols and many others important value added chemicals.[4]

Reduction of carbon dioxide to lower oxidation level using green methodology is a current challenge. Several metal based catalysts have been reported for the reduction of CO_2 where hydrogen was used as reducing agent.[5] Handling of high pressure of H_2 and CO_2 gases are very tough. Thus researchers have found another way to reduce CO_2 using $ZnEt_2$, $AlEt_3$, and hydrosilanes as a reducing agent.[6] Very recently hydrosilanes were used for the formylation of amines and aryl halide via reduction of CO_2. In these reports, CO_2 was converted to the aldehyde oxidation level.[7] Baba et al. and other groups reported the methodology of conversion of CO_2 to formic acid using hydrosilanes.[6e] On the other hand, CO_2 was successfully converted to methanol (alcohol) using various homogeneous and heterogeneous based catalyst.[8] Uptill now, conversion of carbon dioxide to alcohol synthesis is limited to methanol only. Synthesis of higher carbon chain alcohol *via* C-C coupling between substrate and CO_2 is highly desirable. In this context literature study revealed that Yasushi Tsuji et al reported a methodology for the synthesis of homoallylic alcohols from allenes using CO_2 and hydrosilanes as a hydroxymethyl (CH_2OH) source and homogeneous CuCl was used as a catalyst.[4c]

Previously benzyl alcohols were prepared from benzaldehyde or benzoic acid via hydrogenation.[9] Several medicinally important compounds can be prepared from benzyl alcohols such as aliskiren and gastrodin.[10] To the best of our knowledge there is no report on direct transformation of aryl halides to benzyl alcohols *via* CO_2 fixation reaction. Thus, we are first to report a new green methodology for addition of hydroxymethyl (CH_2OH) group onto aryl halides using CO_2 and hydrosilane as a hydroxymethyl (CH_2OH) source, catalyzed by newly prepared Pd nanoparticles embedded nitrogen doped carbon material.

On the other hand, the material that has been used as a catalyst (Pd@N-GMC) is also the first report where nitrogen doped porous material is used as novel support produced from biomass derived glucose as a carbon source and melamine as a nitrogen source and brij-35 was used as a soft template.

Nitrogen doped porous material attracted massive attention as a support of various nanoparticles and has also been used in the field of sensing, drug delivery, adsorption and CO_2 sequestration.[11] Introduction of nitrogen atoms in the carbon material increased the basicity of the material. Simultaneously, presence of nitrogen atom in the carbon materials improved the coordinating property which increased the stability of nanoparicles present in nitrogen doped carbon materials. Furthermore a well-planned nitrogen doped carbon material for the carbon dioxide capture and conversion should have certain necessary characteristics, such as appropriate

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specific surface area and surface high stability, as well as a handy porosity. These properties of nitrogen doped carbon materials improved the catalytic activity. Till now numerous nitrogen doped carbon materials were reported using hard, soft template or without template.[12] Nitrogen doped carbon from biomass derivatives as a carbon source is highly desirable from point view of economical and green prospective. The amount of nitrogen present in the material leads the performance of these materials. When moderate amount of nitrogen is present in the nitrogen doped carbon material, it increases the interaction with carbon dioxide.

Keeping all these factors in mind we have synthesized a novel nitrogen doped carbon material (N-GMC) from glucose and melamine using soft template (brij-35) under hydrothermal treatment. Palladium nanoparticles are doped into porous nitrogen doped carbon material and as the prepared material is porous in nature and contained nitrogen atoms in its porous channel, small sized nanoparticles are well distributed and highly stabilized. The material (Pd@N-GMC) is used as catalyst for the direct synthesis of benzyl alcohols from aryl halides using carbon dioxide and hydrosilane as -CH_2OH source.

2. Experimental Section

2.1 Synthesis of nitrogen doped mesoporous carbon (N-GMC):

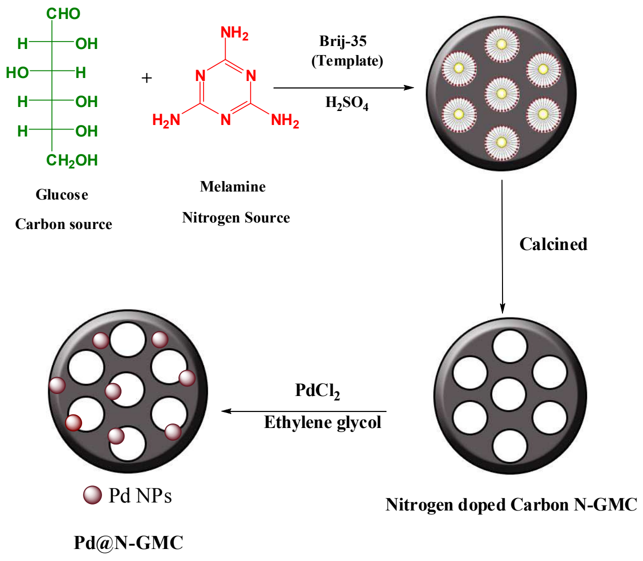
In a typical synthesis, 2 gm of Brij-35 (a polyether and aliphatic hydrocarbon chain surfactant) was dissolved in 0.2M H_2SO_4 aqueous solution (20 mL) and 700 mg melamine was added under stirring for 15h to get a milky suspension. After that 3 gm D-glucose was added to the above emulsion. After being stirred for 30 min at 90 ^{0}C, the mixture was transferred into an autoclave at 403 k for 72h. The brown colored solid product was filtered, washed with water and dried for 24 h at room temperature. The solid product was further calcined at 450 ^{0}C for 2 h in a N_2 atmosphere and final product denoted as N-GMC (Scheme 1).

2.2 Synthesis of nitrogen doped mesoporous carbon embedded palladium NPs (Pd@N-GMC):

500 mg of N-GMC was taken in 50 ml round bottom flask containing 10 ml water. 30 mg $PdCl_2$ was dissolved in 5 ml water and it was added drop wise and stirred for 30 mints. After that water was completely evaporated. Then 20 ml ethylene glycol was added to it and heated at 170 ^{0}C for 6h under stirring condition. After that it was cooled to room temperature then washed with water followed by methanol and dried for 10 h at 80 ^{0}C and denoted as Pd@N-GMC.

2.3 Synthesis of benzyl alcohol from aryl halide:

In a typical reaction, 50 ml high pressure reactor was charged with aryl halide (2 mmol), acetonitrile (5 ml), H_2O (0.4 mL) catalyst (50 mg) and diphenylmethylsilane (6 mmol). Reactor was then charged with CO_2 (1MPa) and heated at 80 ^{0}C for 9 h. After the completion of reaction it was cooled down and gas was released. After that, the organic part of the reaction mixture was separated by extraction with ethyl acetate and water. Reaction mixture was then analyzed by GC equipped with a flame-ionized detector and a capillary column.



Scheme 1 Schematic illustration of the synthesis process of Pd@N-GMC

3. Results and discussion

3.1. Characterization of the Pd@N-GMC

Wide angle XRD analysis of the Pd@N-GMC material is shown in Fig.1a. A broad peak appearing at 26^0 indicate that the nitrogen doped carbon material (N-GMC) that has been used as support for palladium nanoparticles is a graphitic stacking peak. This peak may be assigned to be the reflections from the (002) plane of the N-GMC material. Four other diffraction peaks also appeared at 39.90, 46.60, 68.00 and 81.70 degree corresponding to (111), (200), (220) and (311) reflections planes from crystalline palladium nanoparticles present in the mesoporous N-GMC.[13] Oxidation state of palladium nanoparticle is further determined by XPS analysis (Fig. 1B). Figure 1B shows two Pd 3d peaks at different binding energies. The Pd 3d peaks at 336.1 eV and 341.4 eV corresponding to Pd $3d_{5/2}$ and Pd $3d_{3/2}$ respectively, reveals that in this case, palladium is in zero state.[14]

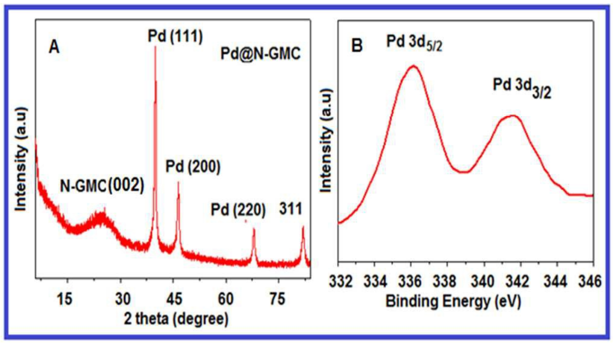


Fig. 1 Wide angle XRD pattern (A) and XPS analysis (B) for PdNPs of the Pd@N-GMC.

FE-SEM image of the material is shown in Fig. 2 which suggests that spherical sized material is connected with each other to form a polymeric nature. The palladium doped carbonized material exhibited approximately the same morphology throughout the

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specimen. The energy dispersive X-ray spectroscopy (EDX) mapping of the material (Pd@N-GMC) shows that carbon, nitrogen, oxygen and palladium elements are present in this carbon matrix (Fig. 3). From EDX analysis it has been found that C: N: Pd (wt.%) ratio is 54:23:9 = 6.0:2.5:1.

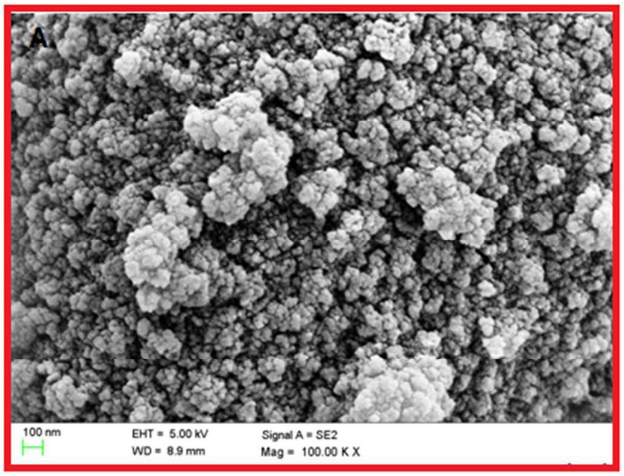

Fig.2 FESEM analysis of the Pd@N-GMC material

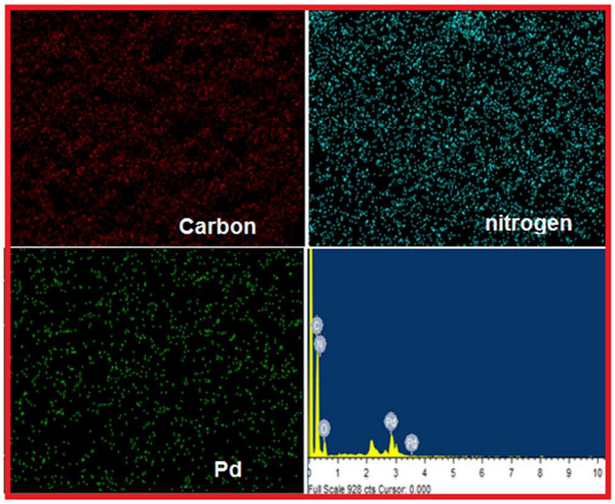

Fig.3 Energy dispersive X-ray spectroscopy (EDX) mapping of the material (Pd@N-GMC)

The morphology of the Pd@N-GMC was analyzed by scanning electron microscope (SEM) and high resolution transmission electron microscopy (HRTEM) analysis. As shown in Fig. 4 spherical natured material is interconnected with each other and average size of the sphere is 80-90 nm. Similar type of observation is also made from TEM images which indicate that spherical natured material contained several pores in its framework (Fig. 4d). During the polymerization, solvent was trapped and this might be the reason behind the creation of void space inside the specimen. Round shaped black spots indicate the palladium nanoparticles which are embedded homogeneously throughout the material (Fig. 4b). The average size of the Pd NPs is close to 8 nm which is clearly observed from HRTEM image (Fig. 4c). The SAED pattern of the palladium nanoparticles embedded material suggests that Pd nanoparticles are crystalline in nature.

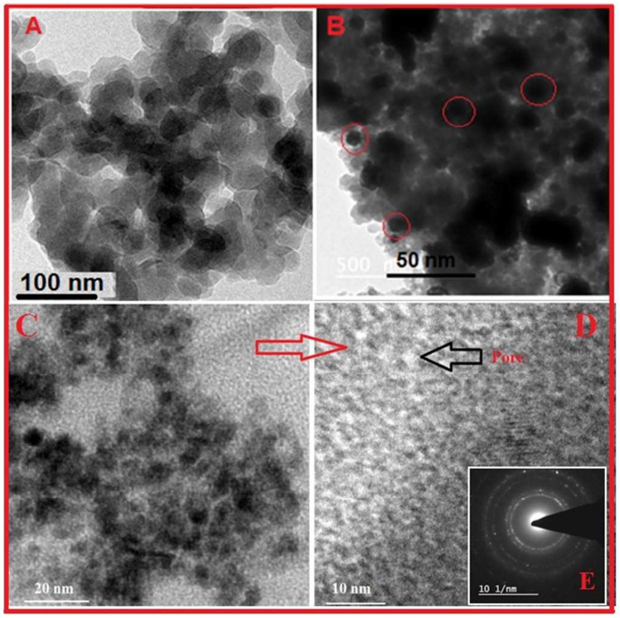

Fig: 4 HRTEM images of the Pd@N-GMC material

N_2-absorption desorption isotherms of Pd@N-GMC material show type-IV curve which indicates the mesoporous nature of the material.[15] As shown in Fig. 5 the BET surface area possess about 337 m^2 g^{-1} and BJH pore size distribution of Pd@N-GMC is centered at 4-5 nm (Fig.S1). On the other hand, the Raman spectroscopy of the material (Pd@N-GMC) is shown in Fig. 6. We have got valuable information about the material from peak position and intensity of the D and G bands. In this analysis mainly two band i.e D and G band are situated at 1375 and 1591 cm^{-1} respectively. The ratio between the D and G (I_D/I_G) is ≈ 0.94. Low intensity ratio indicates the disordered nature of the carbon material due to nitrogen doping.[16]

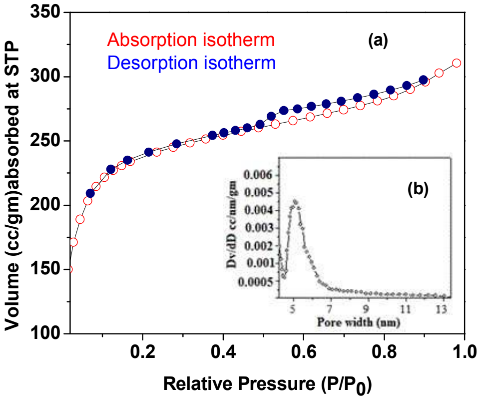

Fig. 5 N_2 absorption and desorption isotherm (a) and BJH pore size distribution (b) of Pd@N-GMC

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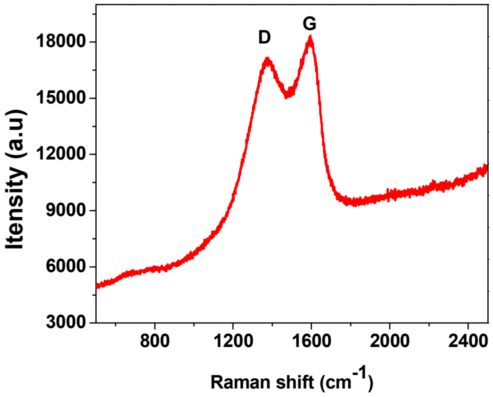


Fig. 6 Raman spectra of Pd@N-GMC material

The thermal stability of Pd@N-GMC in dynamic nitrogen atmosphere was analyzed up to 450 ^{0}C. In Fig. 7 TGA curve shows that material is well stable upto 250 ^{0}C, after that decomposition rate increases and at 400 ^{0}C temperature it undergoes complete decomposition.

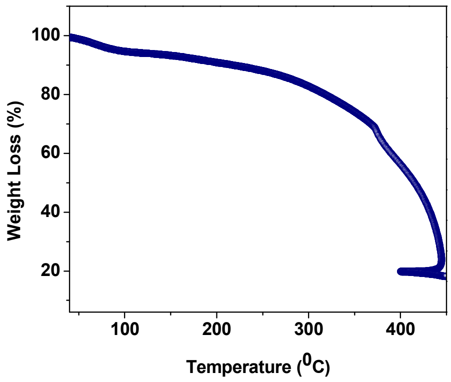
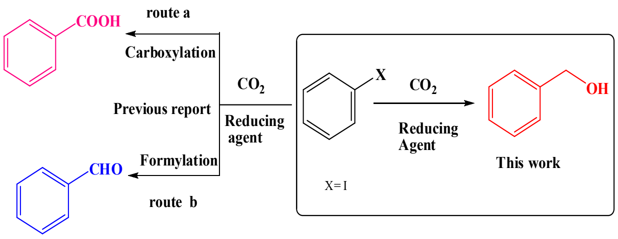


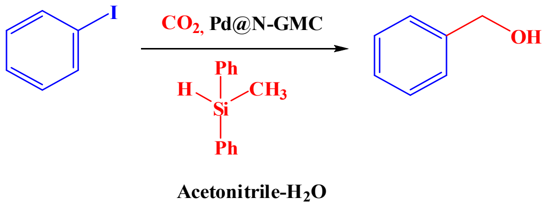
Fig.7 TGA plot of the Pd@N-GMC material

3.2 Catalytic Activity



Scheme 2: Pd catalyzed aryl halide to various transformations

We have designed and synthesized Pd@N-GMC for the above mentioned carbon dioxide fixation reaction. Thus, our initial focus was on feasibility of the reaction i.e transformation of aromatic halide to benzyl alcohol using carbon dioxide and diphenylmethylsilane as a source of hydroxymethyl (CH_2OH) group (Scheme 2). We have taken transformation of iodobenzene to benzyl alcohol as a model reaction under 1 atm CO_2 pressure at 80 ^{0}C in aqueous acetonitrile solvent medium and we have got small amount yield of benzyl alcohol as a product after workup (Scheme 3). To optimize the reaction condition for better conversion of iodobenzene we have screened carbon dioxide pressure, solvent, reaction temperature, reaction time and catalyst amount one by one.



Scheme 3: direct transformation of iodobenzene to benzyl alcohol

In this reaction carbon dioxide plays a crucial role and a vital reaction parameter, thus we have tested the effect of CO_2 pressure by variation of CO_2 pressure upto 1.5 MPa under reaction condition mentioned at Fig. 8. Even at low pressure region of 0.5 MPa CO_2 pressure, we have got interesting results where the yield of benzyl alcohol was almost 60%. But maximum yield of benzyl alcohol (86%) was obtained at 1MPa CO_2 pressure. Beyond this pressure, yield of benzyl alcohol remained same. Similarly, other parameters such as solvent and reaction temperature are also important for this transformation.

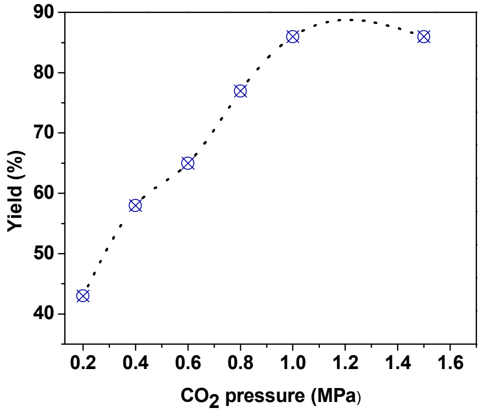


Fig. 8 effect of CO_2 pressure on the reaction

Reaction conditions: iodobenzene (2 mmol), methyldiphenylsilane (6 mmol), catalyst (50 mg), acetonitrile (5 ml), H_2O (0.4 ml), temperature (80 ^{0}C) and 9h.

Effects of solvent and temperature on the reaction are summarized in Table 1 which indicates that acetonitrile and THF gave the higher yield than other polar solvents like DMF and less polar solvent like toluene. In this case trace amount of byproduct such benzyloxymethyldiphenylsilane was obtained but maximum yield of

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benzyl alcohol and lowest byproduct were obtained in acetonitrile medium (ACN) at 80 ^{0}C temperature. At 90 ^{0}C temperature formation of benzyl alcohol remained same, thus all other experiment was done at 80 ^{0}C temperature (Table 1).

Table 1: effects of solvent and temperature on the reaction

Entry	Solvent	Temp. (^{0}C)	Yield^a (%)
1	ACN	80	86
2	THF	80	75
3	DMF	80	59
5	ACN	60	67
6	ACN	70	73
7	ACN	90	84
8	Toluene	80	28

Reaction conditions: iodobenzene (2 mmol), methyldiphenylsilane (6 mmol), catalyst (50 mg), solvent (5 ml), H_2O (0.4 ml), 9h, and CO_2 (1MPa). ^{a}GC yield of alcohol.

We also tested the effect of various supported catalyst and their amount (Table 2) on the reaction. In the absence of catalyst, reaction did not proceed and yield was nil (Table 2, entry 1) which indicates that catalyst is necessary for this transformation. Maximum yield was obtained when catalyst (Pd@N-GMC) amount was 50 mg. In the presence of excess Pd@N-GMC selectivity of benzyl alcohol slightly decreased where small amount byproduct such as C-C coupled product (biphenyl) was formed. Other two catalysts such as Pd@mPMF and Pd@SiO_2 were less effective compared to Pd@N-GMC. Similarly, we have varied the reaction time from 6 h to 10 h but at 9 h maximum yield was obtained (Table 2, entry 4).

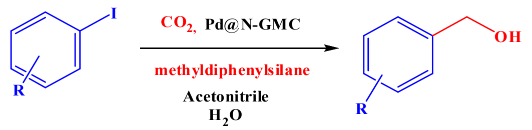
Table 2: effects of catalysts and reaction time on the reaction

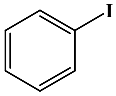
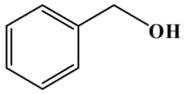
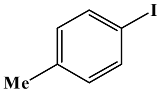
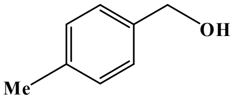
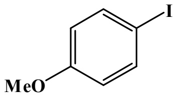
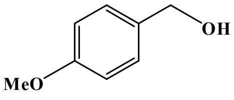
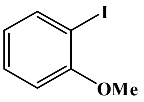
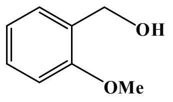
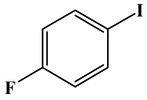
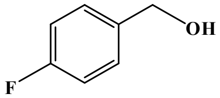
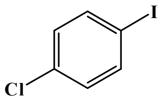
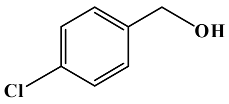
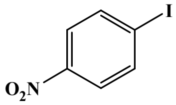
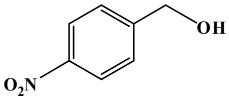
Entry	Catalyst (mg)	Reaction time (h)	Yield (%)^a
1	nil	9	0
2	Pd@N-GMC (30)	9	53
3	Pd@N-GMC (40)	9	67
4	Pd@N-GMC (50)	9	86
5	Pd@N-GMC (60)	9	82
6	Pd@N-GMC (50)	6	58
7	Pd@N-GMC (50)	8	77
8	Pd@N-GMC (50)	10	86
9^a	Pd@mPMF (50)	9	65
10	Pd@SiO2 (50)	9	37

Reaction conditions: iodobenzene (2 mmol), diphenylmethylsilane (6 mmol), Temp. 80 ^{0}C, ACN (5 ml), H_2O (0.4mL) and CO_2 (1MPa). ^{a}GC yield of alcohol. ^{a}mPMF is mesoporous paraformadehyde melamine polymer.

Under optimized condition several aryl halides were tested in this reaction. Surprisingly, we have found that aryl iodides were responding well and produced corresponding benzyl alcohol. No aldehyde product was detected after the completion of reaction under the optimized reaction conditions. But aryl bromide or chloride was not responding in this reaction. Thus, we have varied some electron donating aryl iodides and some electron withdrawing aryl iodides. Both the groups produced moderate to excellent yield of benzyl alcohols. But, in most of the cases it was found that electron donating groups were most effectively converted to benzyl alcohols compared to electron withdrawing groups. Detailed results are given in Table 3.

Table 3: Synthesis of various benzyl alcohols from aryl halides



Entry	Aryl halide	product	Yield (%)^a
1			86
2			90
3			92
4			64
5			80
6			77
7			37

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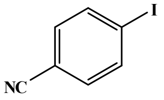
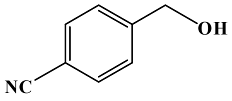
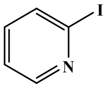
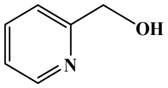
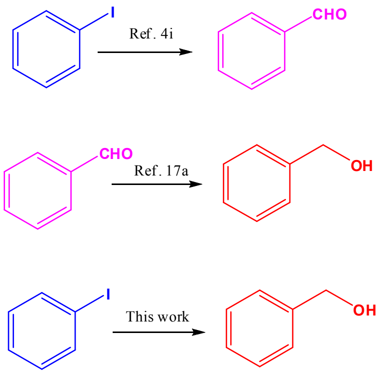
8			45
9			57

Reaction conditions: Aryl halide (2 mmol), methyldiphenylsilane (6 mmol), Catalyst (50 mg), ACN (5 ml), H_2O (0.4ml), Temperature (80 ^{0}C), 9h, and CO_2 (1MPa). ^{a}GC yield of alcohol.

To understand the mechanism behind this reaction and role of nitrogen doped carbon (N-GMC) support and palladium nanoparticles we have studied some literatures and proposed a probable mechanism, although the exact reaction sequence was not determined. As we have used nitrogen doped carbon material where basic nitrogen(s) are present, these nitrogen are able to capture the carbon dioxide and activate it to a formoxysilane intermediate.[4i] On the other side aryl halide undergoes oxidative addition step on PdNPs present in Pd@N-GMC to produce arylpalladium halide which reacts with formoxysilane intermediate and may produce aldehyde product which immediately reacts with diphenylmethylsilane and water to produce direct benzylalcohol as the major product. The product of hydrosilylation of benzyldehyde was detected when reaction temperature was low (< 60 ^{0}C). But at high temperature i.e under the optimized condition no hydrosilylation product was obtained. This proposed mechanism is well supported by some previous reports.[17]



Scheme 4: Iodobenzene to benzaldehyde and benzaldehyde to benzylalcohol stepwise and direct transformation

Recycling Test

In case of supported catalyst, reusability of the catalyst is highly desirable. Thus we have checked the reusability of the reported catalyst, N-MGC. After completion of the model reaction (Table 3, entry 1), the catalyst was removed by simple filtration and washed with methanol and dried at 60 ^{0}C and the same reaction was again performed under similar condition. The conversion and selectivity remained almost same. In this way we have reused the catalyst upto five times with no significant loss of activity (Fig. 9). We have also carried out AAS analysis of the filtrate part of the reaction mixture to confirm that there is no significant metal leaching during the reaction.

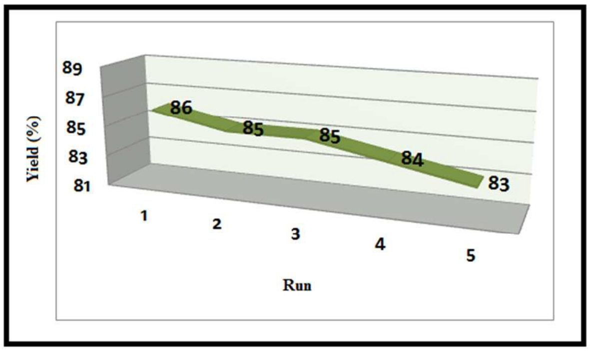


Fig.9 Recycling test of Pd@ N-GMC catalyst

Conclusion

In this work, we report the synthesis of novel palladium nanoparticles embedded nitrogen doped porous carbon material where we have used Brij-35 as a soft template, glucose as a carbon source and melamine as nitrogen source. Palladium nanoparticles incorporated into the surfaces of the material and basic nitrogen present in the material play dual role; one is as stabilizing agent of the palladium nanoparticles and other one is carbon dioxide fixation reaction. The material has been used in the synthesis of benzyl alcohols from aryl halides using carbon dioxide as C1 source. The present catalyst is highly stable. As the starting materials are easily commercially available and inexpensive, it makes the whole process cost effective. On the other hand, the catalyst can be reused for five consecutive cycles with consistent catalytic activity. Further work is in progress to broaden the scope of this catalytic system for other organic transformation.

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Notes and references

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A Route for Direct Transformation of Aryl Halides to Benzyl Alcohols via Carbon Dioxide Fixation Reaction Catalyzed By (Pd@N-GMC) Palladium Nanoparticles Encapsulated Nitrogen Doped Mesoporous Carbon Material

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A nitrogen doped mesoporous carbon material was synthesized from glucose and melamine under hydrothermal treatment. Soft template, brij-35 was used as a template. The palladium nanoparticles embedded porous nitrogen doped carbon material (Pd@N-GMC) was used for the synthesis of benzyl alcohols from aryl iodides via carbon dioxide fixation reaction. The catalyst was highly stable and reusable without any significance loss of its activity.