

Carbon catalyst derived from Himalayan pine for the C-N coupling of organic molecules leading to pyrrole formation

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ABSTRACT

Carbon catalyst consisting of a hybrid structure made up of amorphous carbon and nanographite was prepared from the leaves of *Pinus Roxburghii*. The catalyst was prepared through sodium hydroxide and hydrochloric acid treatment of the dried pine leaves and was further functionalized with sulfuric acid treatment to incorporate the acidic functionalities. The synthesized catalyst was characterized by FTIR, XRD, TEM and XPS spectroscopic techniques and was used as a heterogeneous catalyst for C-N coupling reaction leading to pyrrole formation through the nucleophilic attack of nitrogen atom in amines or imines on the dicarbonyl compounds. The optimized method was explored on various 2,4- and 2,5- dicarbonyl compounds and it was found to afford the five member pyrrole nucleus is good to excellent yields. The scope of the reaction was demonstrated by synthesizing thirteen pyrrole derivatives that are well characterized by IR, NMR and mass spectrometry. The mechanism of the reaction was proposed and acidic sites present on the catalyst surface are believed to be the active sites in the conversion.

Keywords: Carbon material, Heterogeneous Catalysis, Carbocatalysis, C-N coupling, Pyrrole.

1. Introduction

In the past two decades, carbon has been used as an efficient heterogeneous catalyst for developing various synthetic methodologies [1] and the use of nanocarbon has provided a thrust in the field. Activated carbon, carbon nanotubes, fullerene, graphene and nano diamonds have been used in various reactions such as the catalytic reduction of alkenes, dechlorination of alkyl halides and dehydrogenation of aromatic alkanes. Moreover, various hybrid materials involving two or more forms of carbon have been developed to provide enhanced activities. Activated carbon, one of the oldest forms of carbon, has also been utilized for the development of hybrid materials [2]. Different carbon catalysts can be prepared by the physical as well as chemical activation method. The latter is preferred due to lower temperature requirement and provides a higher yield in comparison to physical methods. Sulfonated carbon materials provide another class of solid acidic heterogeneous catalysts that has been explored for various organic reactions [3].

Use of such materials not only provides enhanced yields and recycling of the catalyst, but also offers easy handling of the reaction and mild conditions. *Pinus Roxburghii* is a widespread plant commonly found in the Himalaya at an altitude of 400-2,300 m. Its needles yield oil which is used in soaps, room sprays, and deodorants. Therefore, the leaves of pines are a source of huge waste generated in these industries, which should be utilized further for the development of new materials.

N-containing heterocycles are the very core scaffold of various biologically active compounds, which have gained a plethora of attention as they constitute part(s) of many important organic molecules such as heme, chlorophyll, vitamin B₁₂, alkaloids and co-enzymes. They also possess significant cytotoxicity [4] and have been employed in drug discovery [5] for the development of antitumor [6] and anti-inflammatory agents [7]. They have also been successfully used as herbicides, peptidomimetic, HIV integrase and DNA polymerase inhibitors. The importance of pyrroles has stimulated a great deal of interest for their synthesis involving new methodologies / catalysts. Recently, substituted pyrroles have been synthesized by palladium [PdCl₂, Pd(OAc)₂] [8], magnesium (MgSO₄)

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[9], iron (FeCl₃) [10], platinum (PtCl₂) [11] and zinc (ZnCl₂) [12] based catalysts. Although these metals have the tendency to catalyze the reaction efficiently, their use is not promoted in terms of attaining “sustainability”. Therefore, the development of a milder and more efficient route for the pyrroles synthesis using sustainable/greener alternative to the conventional metal catalyst is required. Due to our ongoing efforts in the catalysis [13] and N-containing heterocycles [14], we prepared a carbon based catalyst from the leaves of pine and used it further for the C-N coupling reaction to synthesize the pyrrole moiety.

2. Experimental

2.1. Materials and methods

The carbon catalyst used in the reaction was prepared from the leaves of *Pinus Roxburghii*. Leaves were collected from Solan (H.P) - India from an altitude of 1502 m. The chemicals used were of analytical grade and were purchased from Sigma Aldrich, which were used without further purification. FTIR analysis was performed on the Agilent Technology FTIR spectrophotometer, using KBr palletes. XPS measurements were carried out using an ultra-high vacuum ESCALAB 250 set-up equipped with a monochromatic Al K α X-ray source (1486.6 eV) anode operating at 15 kV and 20 mA. Deconvolution was performed with XPS peak fit software. Morphology of the catalyst was investigated using Transmission Electron Microscopic (TEM) Analysis [Hitachi (H-7500) model] X-ray maps for the carbon catalyst were obtained on X-ray Diffractometer using powder method on Panalytical's X'Pert Pro model. NMR (¹HNMR and ¹³CNMR) spectra of the synthesized compounds were recorded on Bruker Advance II 400 MHz spectrophotometer. Mass spectra were obtained on Q-ToF Micro Waters Spectrometer.

2.2. Preparation of carbon catalyst

Chemical activation followed by thermal treatment was used to prepare the catalyst from leaves of *Pinus Roxburghii*. The leaves were collected, cut down into small pieces and then dried in sun for 4-5 days. They were then ground to fine particles and dried in hot air oven at 60°C for 24 hrs, washed with N/10 NaOH solution followed by washing with dil HCl (~5M) and re-drying in hot air oven at 60°C for 6 hrs. The raw material (1.0 g) was then heated with sulphuric acid (10mL, 96% w/w) at 100°C for 5 hrs. After cooling the reaction mixture, it was filtered on sintered flask and was washed with distilled water until all the washings were neutral. Finally, the material was dried in hot air oven at 60°C for 12hrs. Finally, it was ground into a

fine powder labeled as C_{DPR} (Carbon derived from *Pinus Roxburghii*), which is used as such in the reaction. The acidic sites determined on the catalyst surface were 0.41 mmol/g.

2.3. Carbon [CDPR] catalyzed C-N coupling

2.3.1. Coupling of 2,4-dicarbonyl compound with ammonium acetate

In a typical protocol C_{DPR} (25 mg, 5 wt% w.r.t benzoin) was added to the mixture of benzoin (500 mg, 2.3 mmol), 2,4- dicarbonyl compounds (2.3 mmol) and ammonium acetate (271 mg, 3.5 mmol) in ethanol (5 mL) and the resulting mixture was refluxed for 70 minutes. Progress of reaction was monitored via the thin layer chromatographic analysis (TLC) and the mixture was filtered in the end to remove the catalyst. The residue was washed with ethanol (2 × 5 mL) and combined filtrate was evaporated under reduced pressure to obtain the crude products, which were finally recrystallized in ethanol to afford pure product.

2.3.2. Coupling of 2,5-dicarbonyl compounds with primary aliphatic / aromatic amines

Hexane-2,5-dione (973 mg, 8.5 mmol) and primary amines (17 mmol) were mixed together in ethanol (5 mL) and C_{DPR} (5 wt% w.r.t 2,5-dicarbonyl) was added to it. The reaction mixture was then refluxed for 70 minutes. The progress of the reaction was monitored via TLC and after completion of the reaction, contents were filtered to remove the catalyst. The residue was washed with ethanol (2 × 5 mL) and the combined filtrate was evaporated under vacuum to obtain the substituted pyrroles.

3. Results and Discussion

Carbon catalyst C_{DPR} was prepared from the pine leaves and the detailed preparation procedure is outlined in the experimental section. In order to detect the acidic functional group, FTIR spectrum of the catalyst was observed. The region between 3500-3000 cm⁻¹ shows two peaks at 3404 cm⁻¹ and 3241 cm⁻¹, which were assigned to hydroxyl functional groups that may present on the surface. The peak at 1505 and 1488 cm⁻¹ may be attributed to the S=O stretching, and the peak at 1148 cm⁻¹ for the C-O vibration of the alcoholic group. Besides, peaks at 1736, 1704, 1687 and 1668 cm⁻¹ (Fig. 1) may be assigned to different -C=O species present on the catalyst surface. Peak at 1620 cm⁻¹ may be assigned to C=C group, which is a part of conjugated system / aromatic ring. This data revealed that the surface of the carbon catalyst most probably has been functionalized with -C=O, S=O, and -COOH groups [15].

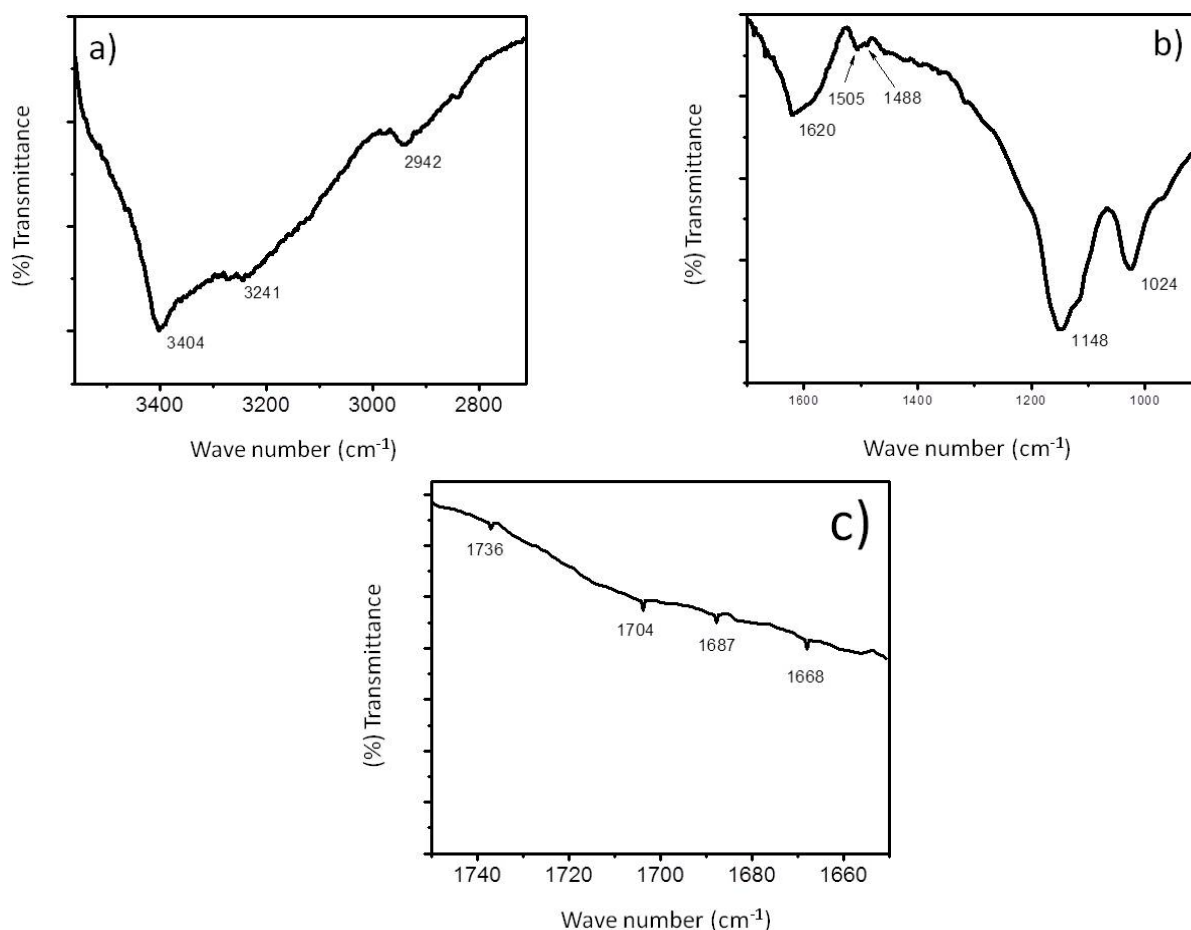


Fig. 1. FTIR of the carbon catalyst showing peaks in 2700-3550 cm^{-1} (a), 900-1700 cm^{-1} (b) and between 1650-1750 cm^{-1} (c).

XRD pattern of carbon catalyst confirms that it is not completely amorphous (Table S1, Fig. 2,) and diffraction peaks at 11.73° , 14.84° , 20.81° , 25.75° , 29.17° , 29.85° , 33.50° , and 49.36° on 2θ scale were observed. The peaks at 11.73° , 14.84° , 20.81° corresponds to the (111), (220) and (222) reflections of the carbon [16,17]. The pattern exhibit peaks at 25.75° similar to intensity (002), signifying high crystallization carbon structure [18]. The peak at 26.80° , 29.17° , 29.85° corresponds to the (100/101) reflection of the carbon, respectively. The peaks at 33.39° , 49.36° at 2θ scale correspond to the graphite nano-domain, respectively embedded in the matrix of activated carbon [19]. The peaks observed at 25.75° and 26.80° corresponding to (002) reflection of carbon evidenced the formation of carbon catalyst C_{DPR} .

The XPS was recorded further and a percentage of different elements along with surface functional groups was derived (Table S2). The analysis revealed that the catalyst surface was rich in carbon with a low percentage of nitrogen functional groups and comparatively very high percentage of oxygenated

groups. The C-1s spectrum was further deconvoluted (Fig. 3a) to probe the nature of the carbon. The peak at 284.4 eV confirms that the catalyst is rich in graphitic carbon content and was in agreement with XRD data. XPS spectrum also shows that the catalyst possesses carbon containing $-\text{COO}-$ functional group. In order to further know the nature of these oxygenated functional groups, the O-1s spectrum was deconvoluted (Fig. 3b). The peak at 532.6 eV confirms the presence of $-\text{COO}-$ functional groups on the surface including the acidic $-\text{COOH}$ group. Finally, the morphology of the catalyst was examined by transmission electron microscopic (TEM) analysis. Fig. 4 shows the TEM images of the catalyst and very small particles ranging from 6.72 nm - 19.8 nm were observed (Fig. 4c). TEM images display the elemental carbon in the form of dispersed near spherical colloidal particles or aggregates similar to that of carbon [20]. The particles appeared roughly in the form of spherical particles (a, b, c) or into randomly branched structures (d) of the spherical particles, and are considered as nano structure because of the range in which they fall.

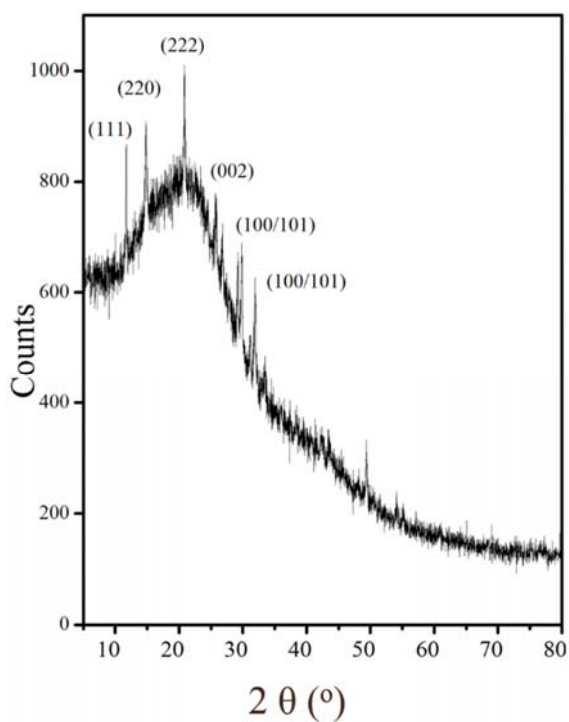


Fig. 2. XRD spectrum of carbon catalyst.

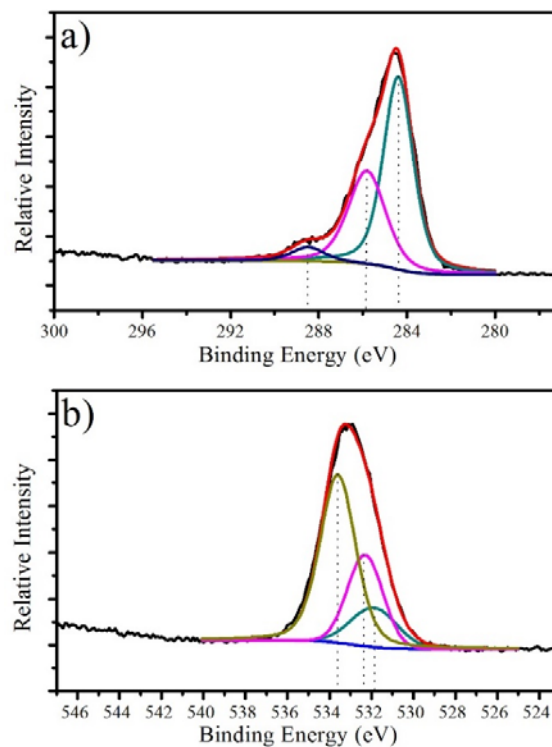


Fig. 3. Deconvoluted C-1s XP-Spectrum (a) and O-1s XP-Spectrum of the catalyst.

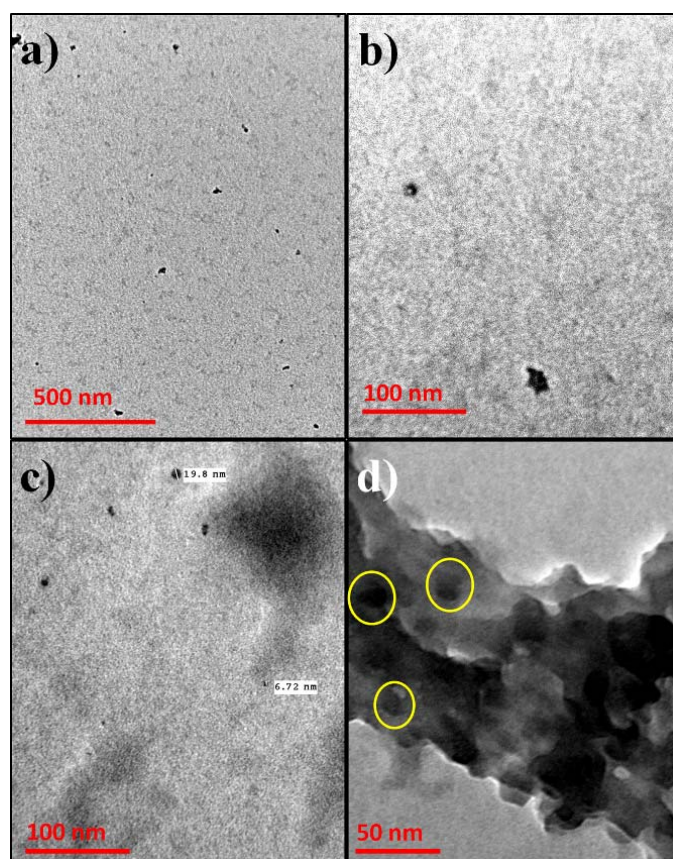


Fig. 4. TEM images of the carbon catalyst.

The prepared catalyst was applied for the C-N coupling reaction leading to pyrrole ring formation. Initially, we tested the pyrrole formation through multicomponent reaction at room temperature (25°C) by adding 5 wt% of the catalyst to the equimolar mixture of benzoin, methyl acetoacetate in ethanol and also by adding ammonium acetate (1.5 mol Eq.) to it (Scheme 1). Progress of the reaction was monitored via TLC analysis and almost complete conversion of reactants was observed after 18h (Table 1). Temperature and time optimization was performed further in order to decrease the reaction time. It was observed that increased yield can be attained in shorter reaction time by refluxing the contents at 78 (± 3) °C (Table 2) and complete conversion was observed after 70 min.

The activity of the catalyst was also compared with the non-catalytic reaction, which comparatively shows very less product yield with longer reaction time (Table 1). The catalyst was also found to be superior in comparison to metal containing analogues, such as ZrOCl₂, ZnCl₂ and MgCl₂ [21]. It also provides comparable yields (Table 3) with other heterogeneous materials such as acidic alumina [22]. The crude product 2-methyl-4,5-diphenyl-1H-pyrrole-3-carboxylic acid methyl ester was isolated after the evaporation of the solvent under reduced pressure and re-crystallized in ethanol to afford the pure product, which was characterized by IR, ¹HNMR, ¹³CNMR and mass spectroscopic analysis.

Table 1. Optimization of reaction temperature.

S. No	Temp. (°C)	Time (h)	Yield (%)
1.	25	18	86
2.	35	0.5	25
3.	45	0.5	38
4.	55	0.5	50
5.	65	0.5	56
6.	78	0.5	68
7.*	78	6	24
8.**	78	1	0

Reaction Condition: all the reactions were carried out using 2.3 mmol of benzoin, 2.3 mmol of methylacetoacetate and 3.5 mmol of ammonium acetate using 5 wt % of activated carbon catalyst in ethanol and the contents were stirred at reported time and temperature (Internal reaction temperature is reported in all cases).

*No catalyst was added during the reaction.

** Reaction was performed in presence of aqueous ammonia.

Table 2. Yield of 2-Methyl-4,5-diphenyl-1H-pyrrole-3-carboxylic acid methyl ester at different time intervals.

S.N.	Time	Yield (%)
1	30	68
2	40	74
3	50	72
4	60	79
5	70	91
6	80	90

Reaction Condition: all the reactions were carried out by refluxing 2.3 mmol of benzoin, 2.3 mmol of methylacetoacetate and 3.5 mmol of ammonium acetate and 5 wt % of activated carbon catalyst in ethanol.

Table 3. Comparison of yield during the synthesis of 1-(2-methyl-4,5-diphenyl-1H-pyrrol-3-yl)ethanone [Product shown in Table 4, S.N. 5].

S. No.	Catalyst	Yield (%)	Solvent/Condition	Ref.
1	C _{DPR}	89	EtOH / Reflux	This work
2	Acidic Al ₂ O ₃	88	EtOH / Reflux	[22]
3	Molybdate sulfuric acid	96	None /80-90 °C	[21]
4	MgBr ₂	85	None / 80-90 °C	[21]
5	CuCl ₂	68	None / 80-90 °C	[21]

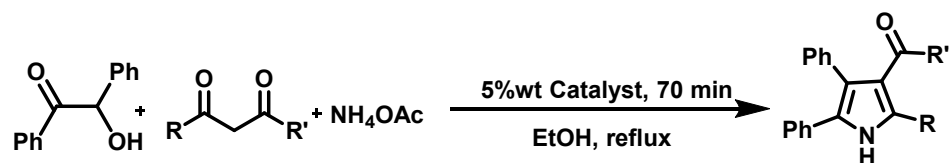
In the FTIR spectrum (Fig. S1) of this compound peak at 3339 cm⁻¹ was assigned to -NH stretching, 1681 cm⁻¹ to C=O stretching, 1439 cm⁻¹ to -C=C stretching, 1181 cm⁻¹ to C-O stretching and 1097 cm⁻¹ to C-N bond formation. Peaks in the region 600-700 cm⁻¹ are due to aromatic rings. ¹H NMR spectrum (Fig. S2) further confirms the formation of pyrrole ring by C-N coupling. Peak at δ 11.2 in the ¹H NMR spectrum is characteristic of NH protons in a cyclic pyrrole ring. Signal at δ 2.5 is characteristic for -CH₃ protons attached to the aromatic pyrrole ring and at δ 3.5 represents -CH₃ protons attached to -COO- group. The Pyrrole ring formation was further ascertained by ¹³C NMR analysis (Fig. S3). Peaks at 112.2 and 123.4 ppm arise due to carbon atoms which are a part of the pyrrole ring and signal at 166.1 ppm confirms the presence of -C=O group in the compound. The mass spectrum (Fig. S4) of this product exhibited a prominent peak at m/z 260, which is 31 units lesser than the molecular mass of this solid. All these analyses confirm the C-N coupling in this multicomponent reaction that generates the pyrrole nucleus. Once the catalyst was utilized towards C-N coupling reaction and the generation of the pyrrole nucleus was confirmed, the scope of this reaction was increased by synthesizing related molecules. The results are compiled in Table 4. The compounds which were prepared have a variety of substituents at position 2- (R) and 3- (R') of the pyrrole ring.

Pyrroles with alkyl, aryl or -OR group at position 2-; and ester, ketonic groups (aliphatic/aromatic) at position 3- were prepared by the developed methodology. Therefore, the catalyst is effective to generate a library of such compounds that can be used as such or functionalized further for other potential applications. The catalyst was recovered in the end by filtration and then stirred in ethanol at room temperature to remove the residual adsorbed compounds. The slurry was filtered and the residue washed twice with ethanol. Recovered C_{DPR} was finally

dried in the oven at 45-50 °C for 16 hrs and then it was tested by the optimized conditions for pyrrole synthesis (via the condensation of benzoin, methylacetoacetate and ammoniumacetate in ethanol). The recovered catalyst exhibited good recycling ability for the consecutive four runs and results are compiled in Fig. 5.

In order to further increase the substrate scope of the reaction, the dicarbonyl was changed to 2,5-dione from 2,4-dione. The nitrogen atom source was also changed from ammonium acetate to primary amines. First, we tested the coupling of benzylamine with hexane-2,5-dione in the presence of 5 wt% of the catalyst in ethanol. The equimolar mixture of both reactants was mixed in ethanol followed by the addition of the catalyst and the resulting mixture was refluxed for 70 min (Scheme 2). The product obtained was characterized by IR and NMR analysis. FTIR spectrum of 1-benzyl-2,5-dimethyl-1H-pyrrole (Fig. S5) does not show peak above 3100 cm⁻¹ due to the absence of -NH protons. Multiple peaks in the region between 3100-3000 cm⁻¹ are due to different aromatic protons present in the molecule. Peak at 1305 cm⁻¹ may arise due to C-N bond and peaks between 1400-1600 cm⁻¹ are indication of C=C in the molecule. The final proof for the pyrrole ring formation was obtained by ¹H NMR analysis (Fig. S6). The peak obtained at δ 6.18 is due to the protons on the pyrrole ring. ¹³C NMR (Fig. S7) shows characteristic peaks at δ 12.3, 46.6, 105.4 that are in accordance with the structure of the pyrrole product. Mass spectrum (Fig. S8) gives the final proof for the pyrrole ring formation where the molecular ion peak is observed at 186.1 m/z corresponding to the molecular weight of 1-benzyl-2,5-dimethyl-1H-pyrrole. We have synthesized other derivatives of pyrroles by this method as listed in Table 5. Pyrroles with different substituents at N atom, ranging from alkyl to aryls bearing both the electron releasing or withdrawing groups were synthesized, in good to excellent yield.

Table 4. C-N coupling of ammonium acetate with benzoin and 2,4-dicarbonyl compounds catalyzed by carbon catalyst.



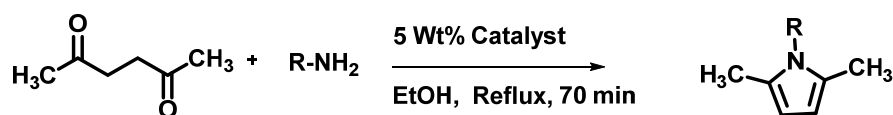
R, R' = alkyl, aryl
Ph = Phenyl

Scheme 1.

S.N	R	R'	Yield (%)
1	-CH ₃	-OCH ₃	91
2	-CH ₃	-OC ₂ H ₅	83
3	-C ₆ H ₅	-CH ₃	90
4	-C ₆ H ₅	-C ₆ H ₅	80
5	-CH ₃	-CH ₃	89
6	-C ₂ H ₅	-C ₂ H ₅	80
7	-OC ₂ H ₅	-OC ₂ H ₅	79

Reaction Condition: 2.3 mmol of benzoin, 2.3 mmol of methylacetoacetate and 3.5 mmol of ammonium acetate and 5 wt % of activated carbon catalyst were refluxed in ethanol.

Table 5. C-N coupling of primary amines with hexane-2,5-dione catalyzed by carbon catalyst.



R = Alkyl, Aryl

Scheme 2.

S.N.	R	Yield (%)
1	-CH ₂ C ₆ H ₅	84
2	-(CH ₂) ₂ CH ₃	80
3	-(CH ₂) ₃ CH ₃	78
4	-(4-CH ₃)C ₆ H ₄	89
5	-(4-NO ₂)C ₆ H ₄	87
6	-(4-Cl)C ₆ H ₄	85

Reaction Condition: 8.5 mmol of Hexane-2,5-dione, 17 mmol of primary amine and 5% wt of carbon catalyst were refluxed in ethanol for 70 min.

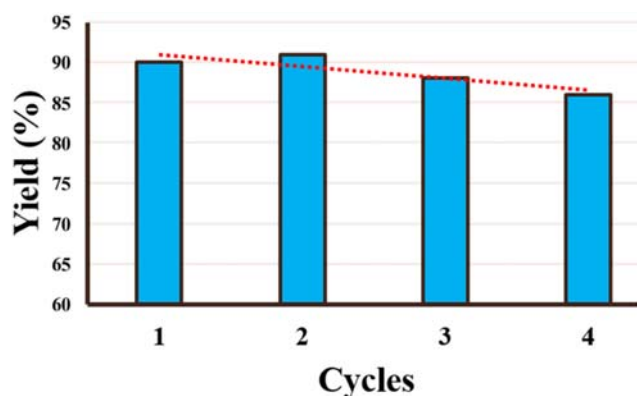


Fig. 5. Recycling of CDPR during the reaction of benzoin, methylacetoacetate and ammoniumacetate by the optimized conditions. Percentage yield of 2-Methyl-4,5-diphenyl-1H-pyrrole-3-carboxylic acid methyl ester (Table 4, S.N. 1) is shown.

The acidic functionalities on the surface of the catalyst are believed to be the active sites in the reaction and operate in a way analogous to other acidic sites [21]. The acidic sites, most probably, are involved in the activation of the carbonyl group in the respective reactants as shown in Fig. 6. In order to check the role of the acidic sites, they are quenched with ammonia and then tested for the reaction under identical conditions. The catalyst (100 mg) was first immersed in ethanol (5 mL) and then 1 mL aqueous ammonia solution was added to it. The mixture was stirred for 16

hrs, filtered and dried in the oven at 60 °C for 7 hrs. The prepared material with quenched acidic sites was used for the reaction of benzoin with methyl acetoacetate under identical conditions and the reactants were not consumed during the reaction under identical condition. The acidic sites are most probably quenched with ammonia by proton exchange and, hence, result in no reaction. To ensure which component gets adsorbed on the catalyst surface, the adsorption study (analogous to our earlier report) was performed [23] in ethanol solution. 100 mg each of benzoin and methyl acetoacetate were dissolved in ethanol (5 mL) to make two separate solutions and 100 mg of fresh catalyst was added into each solution. The contents were filtered under vacuum and the residue was further washed with 25mL (5×5 mL) ethanol. The combined filtrate was evaporated under reduced pressure and then dried at room temperature for 6 hrs. 60% benzoin and 78% methyl acetoacetate were recovered in the end. It clearly indicates that benzoin may show more affinity to stay on surface and its adsorption may start the reaction. The sequence of the reaction steps is shown in Fig. 6. Protonation of benzoin may be performed by the acidic functional groups, which are further attacked by the imine derivative and finally form the pyrrole ring by cyclization. In case of 2,5-dicarbonyl, there is only one carbonyl component, whose activation by acidic group can lead to pyrrole formation.

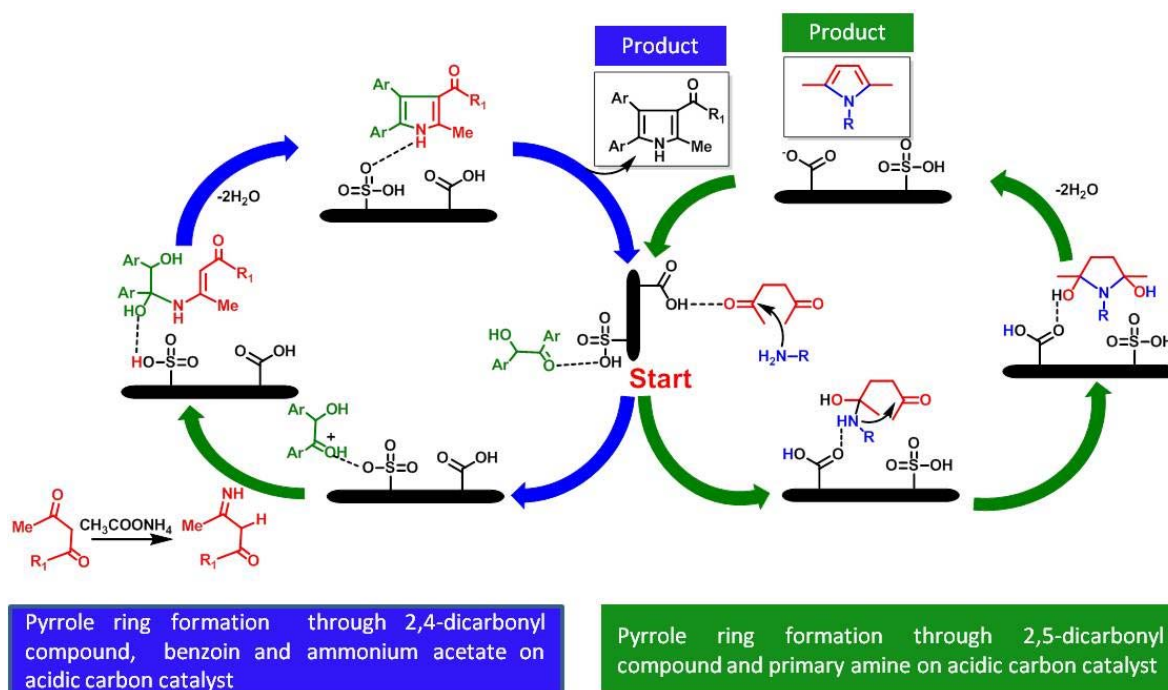


Fig. 6. Probable mechanism for C-N coupling reaction.

4. Conclusion

We have synthesized a sulfonated carbon catalyst by chemical activation followed by the thermal treatment consisting of a hybrid structure containing the amorphous carbon with nanographite embedded in it. It was used for the C-N coupling reaction leading to the pyrrole nucleus formation by two different strategies. In the first strategy, the multicomponent reaction between benzoin, 2,4-dione and ammonium acetate was used for the synthesis of the tetrasubstituted pyrrole ring in the presence of a carbon catalyst. Secondly, the reaction between 2,5-dicarbonyl compound with amines in the presence of the same catalyst was used for making another series of N-substituted pyrrole derivatives. The reaction seems to proceed by the involvement of acidic functional groups, which probably helps in the activation of carbonyl moiety.

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