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A New Atom Economic Approach of Introducing Amine Functionality on a Porous Carbon Surface for Application as an Efficient Base Catalyst

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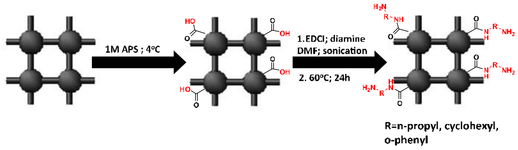
Abstract: Amination of mesoporous carbon nanocage surface has been realized by a novel, atom economic and environment friendly protocol. The aminated mesoporous carbon shows a high activity in the base catalysed synthesis of flavanones.

An upsurge in the research activity around nanoporous carbon materials have recently been observed owing to the potential of these materials as promising candidates as catalytic materials, electrode materials, as well as in the areas of adsorption of large biomolecules, and templates for the synthesis of inorganic metal oxides.(1-4) In spite of immense potential applications, the major drawback which hinders the utilization of these materials in many applications is its poor miscibility with various solvents, especially polar ones like water. Tuning the surface by grafting of functional groups on to these carbon materials therefore play a crucial role in altering the hydrophobic and hydrophilic character, (5) which in turn increases its dispersion in various solvents. This is effective in making these materials useful in catalytic research. The increasing concern over environmental issues and a gradual inclination towards greener methods in catalysis has stimulated the search for solid basic and acidic catalysts which are ideally less toxic, eco-friendly and essentially metal-free. Successful grafting of sulfonic acid groups on to mesoporous carbon CMK-5, forming active solid acid catalysts have been reported.(6) Amine grafting of carbon nanotubes forming solid basic catalysts have also been reported recently.(7) But mesoporous carbon materials have seldom been functionalized by amines to form effective basic catalysts because of the degradation of the structural uniformity of these materials, which takes place in using harsh chemicals or reaction conditions. Mesoporous carbon nanocage, with three-dimentional cage-type pore structures reported recently(8) are highly attractive candidates in various applications due to their high surface areas and larger pore volumes. Even though the introduction of functional groups onto the surface of carbon nanocage is highly crucial due to the fact that the pore walls are much thinner compared to CMK-3, successful oxidative functionalization of these materials without disrupting the mesoporous structure has first been reported by the above authors (8) The importance of amine functionalization of these materials stems from the fact that, it opens up the way of these mesoporous carbons having three-dimentional pore structures with amine groups because these materials have large surface area and a very high specific pore volume to facilitate an efficient and selective catalytic synthesis of bulkier organic molecules in the confined pore spaces.

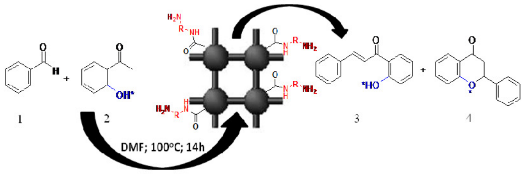
The functionalization of carbon materials with amines is commonly pursued via the initial introduction of the carboxylic acid group and the subsequent conversion of this group into the desired derivative.(9) But the limitation of the above-mentioned process is that, it often utilizes harsh reaction conditions(10) and therefore leads to destruction of the structural integrity of the carbon material. Moreover, this method of amination is multistep, tedious and utilizes hazardous reagents, which on the other hand produce toxic wastes, difficult to dispose. In order to make the process more atom economic and ecofriendly, it is therefore necessary to reduce the number of steps involving separation and purification, as well as to utilize more benign reagents. (11)

The aim of this paper is to demonstrate a novel atom economic, non-toxic, one pot protocol for the introduction of amine functionality to carboxy functionalized mesoporous carbon nanocage. The structural features of the functionalized mesoporous carbon remain intact even though the surface layer of the graphitic chains is disrupted by the functionalization process. The resulting amino functionalized carbon nanocage has vast potential application areas, especially as a metal free basic catalyst in various organic transformations. In this communication the amine grafted mesoporous carbon nanocage has been utilized as a stable, efficient and recyclable solid basic catalyst in the synthesis of flavanones, as flavanone and its derivatives are important intermediates in the synthesis of anticancer, anti-inflammatory, antibacterial, and anti-AIDS drugs.(12)

Scheme 1A shows the method followed for the amine functionalization of mesoporous carbon nanocage, starting from the carboxylic acid functionalized ones. The conventional process is a stepwise one involving a series of reactions with intermediate separation and purifications.(10) It was seen that the mode of bonding on the surface is via an amide bond formation between the acid and the amine. Usually, in an amide coupling reaction an "activated" ester has to be formed to convert it into a better leaving group, for which the carboxylic acid group is converted into acyl chloride and then subsequently into the amide. But in our new protocol, we have utilized dehydrative coupling reagents, carbodiimides such as *N,N'*-Dicyclohexylcarbodiimide (DCC) or 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDCI), which perform the dual role of carboxyl activation by forming an intermediate ester, followed by the abstraction of a water molecule during the attack of the amine group to form the final amide bond. This procedure takes place in a single pot, therefore increasing the efficiency and the atom economy of the process as well as reducing the hassle of repeated work ups and purification. But the use of DCC involved another problem of removal of the byproduct di-cylohexyl urea formed in the process owing to very sparse solubility in any solvent. Therefore clogging of the mesopores of the carbon materials was observed. EDCI on the other hand produces a substituted urea byproduct which is readily soluble in water and can be removed from the surface of the carbon material by simple water wash.(13)



Scheme 1. A) Synthesis of Amine grafted carbon nanocage.



Scheme 1. B) Synthesis of flavanone by Claisen Schmidt condensation.

Carbon nanocage was subjected to amination by three different amines viz. 1, 2 diaminopropane, 1, 2 diaminocyclohexane, 1, 2 phenylenediamine to form three different catalysts viz. CNC-PN, CNC-CYC, CNC-OPD respectively. In order to relate the structure to reactivity these catalysts were tested in the Claisen–Schmidt condensation between 2-hydroxyacetophenone and benzaldehyde and subsequent isomerization of the hydroxychalcone intermediate to form flavanone (**Scheme 1B**).

All the catalysts are studied by FT-IR spectroscopy in order to determine chemical linkage of amine to the surface of the carbon nanocage (Fig.1).

Table 1. Textural parameters and elemental composition of the amine functionalized carbon nanocage

sample	SA	PD	PV	C%	N%	O%
CNC-PN	261.7 (470)	3.36	0.244	63.6 (72.9)	9.28 (9.08)	21.0 (18.19)
CNC-CYC	346.3 (470)	3.73	0.361	67.0 (76.0)	8.87 (8.49)	18.4 (15.5)
CNC-OPD	359.9 (470)	3.72	0.390	67.7 (75.6)	9.90 (9.38)	17.9 (14.99)

[a] Unfunctionalized carbon surface area in the parenthesis of column 2.

[b] Atomic percentage of elements in the parenthesis, The composition is obtained by X-Ray photo electron spectroscopy (error margin ± 2%, owing to factors such as uncertainties in the compositions of the standards and errors in the various corrections which need to be applied to the raw data)

SA=Surface area
PD=Pore diameter
PV=Pore Volume

The broad peak in the IR spectrum of the samples in the range of 3266-3430cm^{-1} includes the bands for free NH_2 stretch and N-H stretch, while the peak around 3175 cm^{-1} in CNC-PN, 2940 cm^{-1} in CNC-CYC and 2933cm^{-1} in CNC-OPD indicates the C-H bond stretching of the amine bound alkyl or aryl group. The sharp bands around 1593cm^{-1} and 1533 cm^{-1} indicates the stretching of C=O group and bending of N-H bond. The band arising due to C-N stretch is seen around 1220cm^{-1}. Elemental analysis of the samples gave the exact atomic percentages of each element present, which provides a clear picture of the extent of amine binding taking place in each sample (Table 1).

Thermogravimetric analysis (not shown here) showed the decomposition temperature to be much higher than the boiling points of the respective amines, thus confirming a stable bond formation. Moreover, the peak around 100˚C, shows that a considerable amount of physisorbed water is released from the surface of the amine functionalized CNC. This indicates that a hydrophilic character has also been successfully incorporated into the material. The peak around 300˚C shows a loss of about 21% weight loss, which can be attributed to the amine. This again is significant in case of mesoporous carbon as only a surface grafting can be affected keeping the textural properties of this thin walled carbon intact. From the XPS data the amount of amine grafted in each case is approximately about 0.05g per gram of carbon.

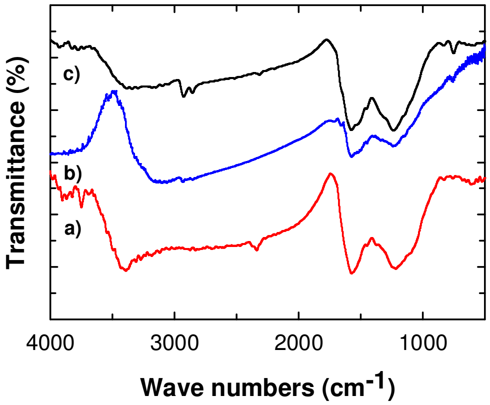


Fig. 1. FT-IR of amine functionalized carbon nanocage a) CNC-PN b) CNC-CYC c) CNC-OPD

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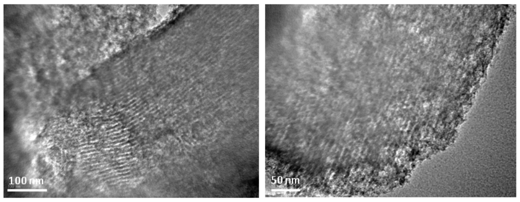

Fig. 2. Transmission electron micrographs of CNC-CYC

The retention of the mesoporous structural order in the amine functionalized carbon nanocage was investigated by transmission electron microscopy (Fig. 2). The micrographs recorded in two different crystallographic directions indicate that a considerable amount of disorder had crept in by the grafting process. This can be explained in terms of the wall thickness of carbon nanocage being much lesser than the hexagonal mesoporous carbons. But although structural collapse has been observed to a certain extent, the long-range periodicity and the ordered arrangement of the mesoporore have been found to be maintained grossly. This has been well supported by the Nitrogen adsorption isotherm, pore size distribution low angle X-Ray diffraction. The nitrogen adsorption isotherms of CNC-PN, CNC-CYC and CNC-OPD and their corresponding BJH desorption pore size distribution are shown Fig. 3 and 4. The isotherms of all the samples are found to be of type IV according to the IUPAC classification and exhibit an H2 hysteresis loop. This again indicates that the overall ordered structure of a mesoporous carbon nanocage is well maintained in spite of a minor disorder being incorporated during the process of grafting. The drastic reduction of surface area of the amine-functionalized samples (Table 1) compared to the parent carbon nanocage corroborates the above point. From the pore size distribution data of the aminated samples it was found that the diameters and the corresponding pore volumes decreased significantly after the grafting process. This can be explained by the fact that a partial destruction of textural uniformity has definitely taken place in the course of an oxidation of the surface carbon atoms in the pore channels followed by the attachment of the diamines. Some amount of pore blockage can also be expected by the presence of the amines in the pore spaces. This phenomenon is more pronounced in case of CNC-PN, as it has a pendant alkyl amine chain that in the case of the other two. Further the low angle X-ray diffraction patterns of the amine functionalized carbon nanocage samples show a distinct but a slightly broadened out peak for the 111 plane while the peaks for 200 and 220 planes are heavily broadened. This also supports the above-mentioned fact that the overall structure of carbon nanocage is grossly maintained in the amine functionalized samples in spite of a minor structural disorder being present. The unit-cell constant is found to increase from that of the pristine carbon nanocage, but remains almost the same with that of the oxidized one. In this context it may be mentioned that the oxidation step of the functionalization of carbon nanocage is the most critical one, as even a minor over oxidation can collapse the

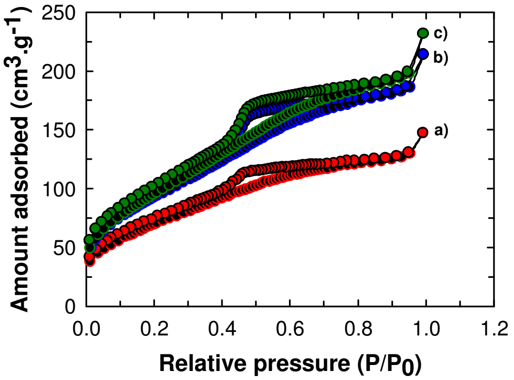

Fig. 3. Nitrogen adsorption isotherms of amine functionalized carbon nanocage a) CNC-PN b) CNC-CYC c) CNC-OPD.

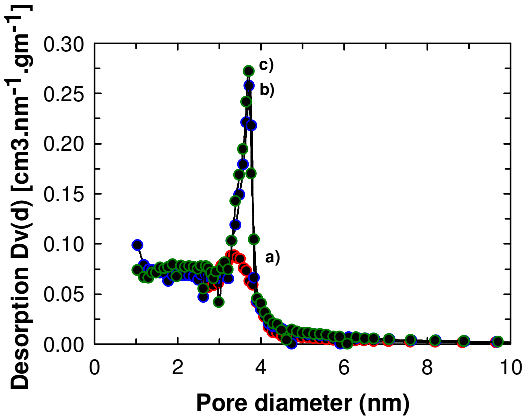

Fig. 4. Pore size distribution of carbon nanocage a) CNC-PN b) CNC-CYC c) CNC-OPD.

whole structural integrity of the carbon nanocage unlike in case of CMK-3, which is much more robust and resistant to oxidation due to its greater wall thickness. But the textural properties of carbon nanocage such as greater surface area and pore volume are indispensible in the area of catalysis, which attracted us to undertake its functionalization.

This new class of solid catalysts was expected to exhibit not only an improved product conversion, but also to improve the selectivity towards the formation of the desired product by selective diffusion and mass transfer through the pore channels. Relating structural features to the reactivity, it was found that catalytic synthesis of the flavanoids from benzaldehyde and 2-hydroxyacetophenone are carried out via a Claisen Schmidt condensation followed by an intramolecular Michael addition (Scheme 1B) very efficiently in the confined pores of the functionalized carbon nanocage. Among the three different amines used, the activity of the carbon nanocage functionalized with 1, 2 phenylenediamine was least active. This can be explained in terms of the decreased basicity of the aromatic amines, even though from the elemental analysis the amount of amine attachment was found to be the greatest in case of the above mentioned (Table 1). The best yield of the product was obtained when CNC-PN was subjected to catalyze the reaction. This phenomenon occurs due to the fact that even though the amount of amine grafted in case of CNC-PN is lesser than in the case of CNC-OPD, The basicity of the later is much greater. The greater activity of CNC-PN over CNC-CYC can be explained in terms of comparatively lesser amount of amine groups being attached in case of CNC-CYC. This can again be explained due to the fact that linear alkyl amines possess greater nucleophilicity, due to which the formation of amides becomes more facile in the case of CNC-PN. Thus, even though the basicity of both the amines is comparable, the number of amine groups grafted on the surface is lesser in case of the later. A greater conversion to the desired flavanone product is also found when CNC-PN was used as a catalyst. This result can be explained based on the short chain length of 1, 2 diaminopropane inside the pore channel, which gives adequate room for the rapid diffusion and mass transfer of bulkier molecules. Therefore in similar lines it was seen that 1, 2 phenylene diamine grafted carbon nanocage, having much smaller pore diameter gave 2-hydroxychalcone as the major product. The reaction was found to yield better result in presence of a solvent than in absence of it. This may be explained from the fact that presence of a solvent facilitates the diffusion of the substrates through the pore channels of the amine grafted carbon nanocage (Table 1).

The reactivity and the selectivity of the catalyst were compared to widely used commercially available magnesium oxide. Though a high conversion of the reactants is also obtained in case of the above-mentioned catalyst our method proved to be better in selectivity towards the desired flavanoid product.

Recyclability experiments were carried out in order to study the stability of the catalyst. Three consecutive cycles of the reaction were run using CNC-PN as the catalyst. It was found that a minor reduction of yield was found in each cycle. This reduction of the yield may be attributed to the inevitable minor loss of catalyst during separation after each cycle. The filtrate after the removal of the catalyst was subjected to GC to identify any leached out amine species from the pore channels. But it was found that the amine moieties bound by covalent amide bonds to the surface of the carbon nanocage were stable and no major leaching of amines were detected.

Experimental Section

The CNC was subjected to oxidation according to the reported procedure.(8) The surface oxidized CNC-COOH was then treated with a 1M solution of EDCI at room temperature for 1h to form the intermediate ester followed by addition of the amine (1g) in DMF and stirring at 60^0C for 8h. The resulting product was separated and washed several times with water and finally with acetone to get rid of the excess EDCI and amine. The resulting powder was then dried under reduced pressure at room temperature.

General procedure for the synthesis of dibenzyls and alkyl phenyl propionates

The catalytic reactions were perfomed according to the procedure reported.[11] The compounds were identified by matching the analysed data with that of the reported ones.[11]

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