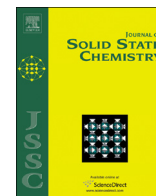




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journal homepage: www.elsevier.com/locate/jsscA facile approach towards increasing the nitrogen-content in nitrogen-doped carbon nanotubes *via* halogenated catalystsL.M. Ombaka^a, P.G. Ndungu^{a,b}, B. Omondi^a, J.D. McGettrick^c, M.L. Davies^c, V.O. Nyamori^{a,*}^a School of Chemistry and Physics, University of KwaZulu-Natal, Westville Campus, Private Bag X54001, Durban 4000, South Africa^b Department of Applied Chemistry, Doornfontein Campus, University of Johannesburg, P.O. Box 17011, Johannesburg 2028, South Africa^c SPECIFIC, Swansea University, Baglan Bay Innovation Centre, Baglan, Port Talbot SA12 7AX, United Kingdom

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ABSTRACT

Nitrogen-doped carbon nanotubes (N-CNTs) have been synthesized at 850 °C *via* a CVD deposition technique by use of three ferrocenyl derivative catalysts, i.e. *para*-CN, -CF₃ and -Cl substituted-phenyl rings. The synthesized catalysts have been characterized by NMR, IR, HR-MS and XRD. The XRD analysis of the *para*-CF₃ catalyst indicates that steric factors influence the X-ray structure of 1,1'-ferrocenyldiacrylonitriles. Acetonitrile or pyridine was used as carbon and nitrogen sources to yield mixtures of N-CNTs and carbon spheres (CS). The N-CNTs obtained from the *para*-CF₃ catalysts, in pyridine, have the highest nitrogen-doping level, show a helical morphology and are less thermally stable compared with those synthesized by use of the *para*-CN and -Cl as catalyst. This suggests that fluorine heteroatoms enhance nitrogen-doping in N-CNTs and formation of helical-N-CNTs (H-N-CNTs). The *para*-CF₃ and *para*-Cl catalysts in acetonitrile yielded iron-filled N-CNTs, indicating that halogens promote encapsulation of iron into the cavity of N-CNT. The use of acetonitrile, as carbon and nitrogen source, with the *para*-CN and -Cl as catalysts also yielded a mixture of N-CNTs and carbon nanofibres (CNFs), with less abundance of CNFs in the products obtained using *para*-Cl catalysts. However, *para*-CF₃ catalyst in acetonitrile gave N-CNTs as the only shaped carbon nanomaterials.

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1. Introduction

Shaped carbon nanomaterials (SCNMs) such as carbon nanotubes (CNTs) are fascinating carbonaceous materials with novel physical and chemical properties [1]. Owing to their unique properties, such as high tensile strength, Young's modulus [2], thermal stability [3], surface area [4], and excellent electrochemical properties [5], CNTs have been found to be useful materials in the field of nanotechnology [1]. These physicochemical properties of CNTs can be enhanced further *via* nitrogen-doping to form nitrogen-doped CNTs (N-CNTs) [6]. The nitrogen species present in N-CNTs act as n-type conductors and as basic functional groups thus enhancing the electrical properties [7] and surface energy [8] of N-CNTs. Additionally, N-CNTs contain defect sites that can improve their wettability and surface area [9] which are useful properties for potential application of N-CNTs in various fields such as catalysis [1] and field emission devices [10].

Unlike other flake-like carbonaceous materials such as graphene, CNTs and N-CNTs are cylindrical and contain hollow

cavities in their structures. These hollow cavities can be filled with iron to form ferromagnetic CNTs and N-CNTs [11]. Ferromagnetic CNTs and N-CNTs are used in different areas, such as electromagnetic wave absorption [11]. They can also be applied as heterogeneous catalysts with the added advantage of the ease of separating them from solutions by use of magnets [12]. Iron filled CNTs have been synthesized by using mixtures of organic halogens and ferrocene as catalysts [13]. For instance, Gui et al. synthesized iron-encapsulated CNTs by use of dichlorobenzene and ferrocene catalyst [14]. However, little is known about the use of halogenated ferrocenyl derivatives as catalysts in the synthesis of iron encapsulated CNTs or N-CNTs.

Ferrocene [15] and ferrocenyl derivatives [16], due to their volatile nature, are frequently used as catalysts in the synthesis of CNTs and other shaped carbon nanomaterials (SCNMs) [15,17]. Nitrogen-containing ferrocenyl derivatives, as catalysts, have been explored in the synthesis of N-CNTs [8]. In some instances, the use of nitrogen-containing ferrocenyl derivatives yields N-CNTs with better physical or chemical properties as opposed to the use of ferrocene dissolved in a nitrogen containing organic solvent. For example, Nxumalo et al. showed that the use of 4-ferrocenylniline as a catalyst yields N-CNTs with higher nitrogen-doping levels

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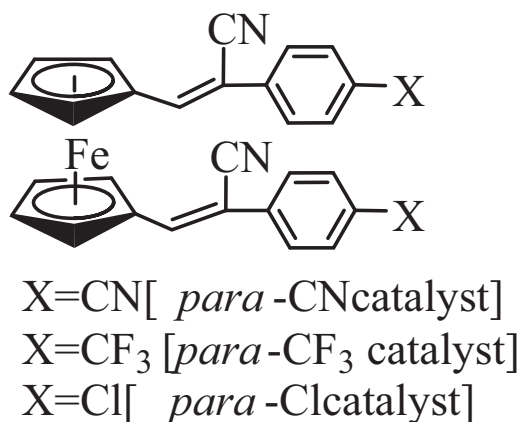


Fig. 1. Structure of 1,1'-ferrocenyldiacrylonitriles used as catalysts.

compared with ferrocene in aniline solution [18]. Another seldom-explored approach that can also be useful in modulating the nitrogen content and species in N-CNTs and other properties of SCNMs is the use of halogens [19]. Halogens, such as fluorine, are potential oxidizing agents that could induce defects in CNTs during the nucleation; these defect sites can easily accept nitrogen species resulting in higher nitrogen-doping levels. However, reports on the use of halogens to modulate nitrogen-content in N-CNTs are limited.

In this study, 1,1'-ferrocenyldiacrylonitriles (Fig. 1), containing nitrogen-(*para*-CN), fluorine- (*para*-CF₃) and chlorine-heteroatoms (*para*-Cl), were synthesized and characterized. The X-ray crystallographic structure of the *para*-CF₃ catalyst is reported for the first time. The 1,1'-ferrocenyl-diacrylonitriles have been investigated as novel catalyst for the synthesis of N-CNTs, carbon nanofibres (CNFs) and carbon spheres (CS). The chlorine and fluorine heteroatoms were used to evaluate the effect of halogenated catalysts on nitrogen-doping and iron encapsulation into the cavity of N-CNTs. We also present the effect of halogen heteroatoms on the diameters, type of nitrogen-species in N-CNTs and also the not only on amount of product but also the distribution of the products. The effect of varying the carbon and nitrogen source has been evaluated by using either acetonitrile or pyridine as the carbon and nitrogen source.

2. Results and discussion

2.1. Synthesis of *para*-CN, *para*-Cl and *para*-CF₃ catalysts

Synthesis of *para*-CN, *para*-Cl and *para*-CF₃ substituted catalysts was conducted as reported by Ombaka et al. [20]. Grinding together 1,1'-ferrocenedicarboxaldehyde and the substituted phenylacetonitriles in the presence of a drop of piperidine yielded the *para*-CN, *para*-Cl and *para*-CF₃ substituted catalysts as depicted in Scheme 1 [20]. The reaction mixture readily turned into a melt or a gum upon grinding at ambient temperatures. The obtained melt or

gum was dried under vacuum and IR and ¹H-NMR spectroscopy were used to confirm the reaction completion.

2.1.1. Crystal structure of the *para*-CF₃ catalyst

We have previously reported the synthesis and characterization of the *para*-CF₃ catalyst [20], however, the crystal structure of this catalyst has not been reported. The molecular structure and atom numbering scheme of the *para*-CF₃ catalyst is presented in Fig. 2. Selected bond distances and angles of the *para*-CF₃ structure are summarized in Table 1. The crystal structure of the *para*-CF₃ catalyst contains a more bulky -CF₃ group on the *para*-position as opposed to the *para*-CN and *para*-Cl groups in the previously reported catalysts [20].

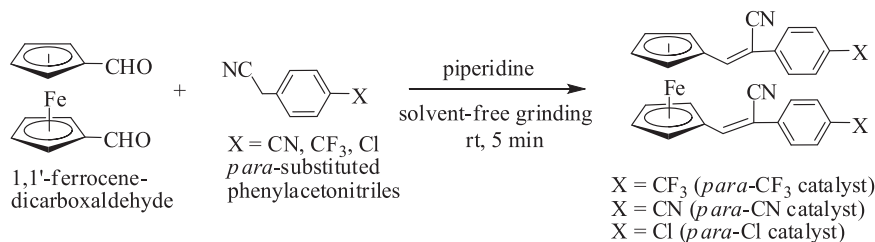
The bulky -CF₃ group does not seem to affect the arrangement of the two *para*-(trifluoromethyl)phenylacrylonitrile moieties since the structure adopts a *cisoidal* conformation which is observed in less bulky groups (*para* -CN and -Cl) that have been previously reported [20]. However, the two -CF₃ groups seem to influence the conformation around the C₁₁-C₁₃ and C₂₀-C₂₂ double bond in which the CN groups are observed to face opposite directions. The steric strain caused by the -CF₃ groups also tends to influence the cyclopentadienyl rings which are staggered by an angle of 17.9° from an ideal eclipsed geometry. The staggering angle in the *para*-CN and *para*-Cl were smaller (15.85° and 0.654°, respectively) [20].

All Fe-C bond distances and angles are well within the expected ranges of similar ferrocenyl derivatives [20]. In the *para*-CF₃ catalyst, the cyanoethyl benzonitrile groups are staggered by an angle of 170.5(4)° while, in the *para*-CN and -Cl catalysts the cyanoethyl benzonitrile groups were staggered by 165.86(18)° and 156.3(4)°, respectively [20]. As the *para*-substituent increases in size (*i.e.* Cl < CN < CF₃), the angle by which the cyanoethyl benzonitrile groups are staggered also increases. The increase in steric strain could be perpetuated by repulsive interactions between the two cyanoethyl benzonitrile groups resulting in a wider angle of staggering.

2.2. Effect of the *para*-substituent and nitrogen source on SCNMs

In this section, the SCNMs synthesized by using the *para*-CF₃, -CN and -Cl catalysts are named as SCNMs-F, SCNMs-CN and SCNMs-Cl, respectively. In a similar manner, the N-CNTs obtained by use of *para*-CF₃, -CN and -Cl catalysts are named as N-CNTs-F, N-CNTs-CN, and N-CNTs-Cl, respectively.

Product yields obtained from all three catalysts dissolved in pyridine and acetonitrile are summarized in Table 2. Amongst the three catalysts used, the *para*-CF₃ catalyst gave the highest yield with pyridine or acetonitrile. The fluorine in *para*-CF₃ catalyst may have restructured the iron catalysts to a more active phase of higher carbon solubility hence increasing the yield of SCNMs [21]. The *para*-Cl catalysts gave the lowest yield with pyridine and acetonitrile. A previous report also observed that chlorinated catalysts lower the growth rate of SCNMs [22], this may be attributed to reactions between the catalysts active sites and chlorine which deactivate the catalysts thus decreasing the yield [23].



Scheme 1. Mechanochemical synthesis of 1,1'-ferrocenyldiacrylonitriles under solvent-free conditions.

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