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Application of heteroatom-containing iron(II) piano-stool complexes for the synthesis of shaped carbon nanomaterials

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ABSTRACT

Based on iron(II) piano-stool complexes, five compounds were synthesized by varying the organo-heteroatom ligands in their structure. Two different heteroatoms were considered, namely, nitrogen and sulfur, as constituents of the ligands on the complexes. Compounds **1** and **2** contained the nitrogen heteroatom in their ligands whilst **3** to **5** contained sulfur. These compounds were used as catalysts in the synthesis of shaped carbon nanomaterials (SCNMs) by means of the floating catalyst chemical vapour deposition method (CVD). The nitrogen-containing catalysts produced nitrogen-doped carbon nanotubes (N-CNTs) with bamboo morphology. On the other hand, the sulfur-containing catalysts produced mainly carbon spheres (CS) and some amorphous carbon (AC) as the bulk of the resulting SCNM products. In the case of compounds **1** and **2**, higher nitrogen content and reaction temperatures were shown to promote nitrogen-doping which led to more disordered N-CNTs and an increase in the outer diameter of the N-CNTs. In the case of compounds **3** to **5**, higher reaction temperatures led to more graphitic CS and an increase in the average diameter of the CS. The various results and analyses show that the synthetic variations of not only reaction conditions, but also the type of substituent on the organometallic catalyst ligand and its structure, can lead to a level of control towards the resulting carbon nanostructures.

Introduction

Shaped carbon nanomaterials (SCNMs) display interesting properties that are closely related to their shapes and sizes. Hollow or filled carbon spheres (CSs), carbon nanotubes (CNTs) and fullerenes, amongst other SCNMs, have been shown to have interesting properties and applications across most scientific and technological fields [1,2]. Some of the properties exhibited by SCNMs include high surface areas, which permit applicability in areas such as catalyst supports [3,4], gas adsorption [4,5] and water purification systems [6,7]. Whilst the formation mechanisms of SCNMs is still a fascinating phenomenon [8], the synthesis procedures require a certain level of control towards the desired products and their dimensions.

SCNMs can be synthesized by a variety of techniques which include chemical vapour deposition (CVD) [9], laser ablation [10] and arc discharge [11]. Amongst the three, CVD has proven to be the most facile method that can be made selective towards the production of a particular SCNM [12]. A greener CVD method that has been used involves the introduction of a catalyst and any other reactant/s into a closed environment (autoclave), which is then heated under autogeneous conditions. This technique avoids the use of a catalyst support and eliminates the related difficult and expensive support removal procedures [13].

The addition of heteroatoms during the synthesis of SCNMs by the CVD method is one way to improve the selectivity and yield towards specific SCNMs [14]. Depending on the heteroatom introduced, the carbons on the structure of the SCNMs can be replaced with the added heteroatom, as a dopant. This can be achieved by the addition of a heteroatom-containing carbon source, heteroatom-containing catalysts or a combination of both approaches.

The use of nitrogen-containing compounds has been shown to result in the incorporation of N-atoms and the production of nitrogen-doped CNTs (N-CNTs) [15–19]. N-CNTs display a "*bamboo-like*" morphology because of the disorder introduced by the nitrogen [17]. The extent or level of nitrogen-doping in N-CNTs is related to the distances (segmental length) of the bamboo compartments [18]. The nitrogen atom in N-CNTs may also serve as a functionalization point for the introduction of a number of other functional groups.

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Sulfur is another heteroatom that has been introduced during SCNM synthesis by means of the CVD method [20]. Unlike nitrogen, a dopant, sulfur has been reported to act as a promoter when introduced during the synthesis of SCNMs [21]. Hence, the sulfur atom is not incorporated into the structures of the SCNMs but has been shown to increase yields [14] and improve selectivity towards certain types of SCNMs [8,9]. For example, sulfur as an additive, has been known to introduce Y-shaped CNTs and aid in the formation of helical carbon nanotubes (HCNTs) [22]. In addition, the presence of sulfur, during the synthesis of SCNMs *via* the CVD method, has been shown to enhance the encapsulation of ferromagnetic moieties, thus improving the soft magnetic properties of the CNTs, making them suitable for applications in electromagnetic devices.

Owing to their volatile nature, organometallic compounds are commonly used as catalysts in the synthesis of SCNMs *via* the CVD method [23]. A good example of such organometallic compounds is iron pentacarbonyl, $Fe(CO)_5$, which has been successfully used to synthesize SCNMs [23]. The use of polymers containing organometallic complexes to provide a metal source for CNT synthesis has also been reported to yield a controlled production of CNTs [24,25]. However, there is need to explore a wider scope of catalysts to deepen the understanding of catalyst structure-product property relationships. In the past, we have synthetically modified ferrocene to incorporate a variety of ligands that alter the catalyst properties and thus alter the properties of resulting SCNMs [19,26,27]. Incorporation of heteroatoms directly into the ligands of the catalyst has also been shown to be a more effective way of modifying the SCNMs produced compared to their introduction as external dopants [28].

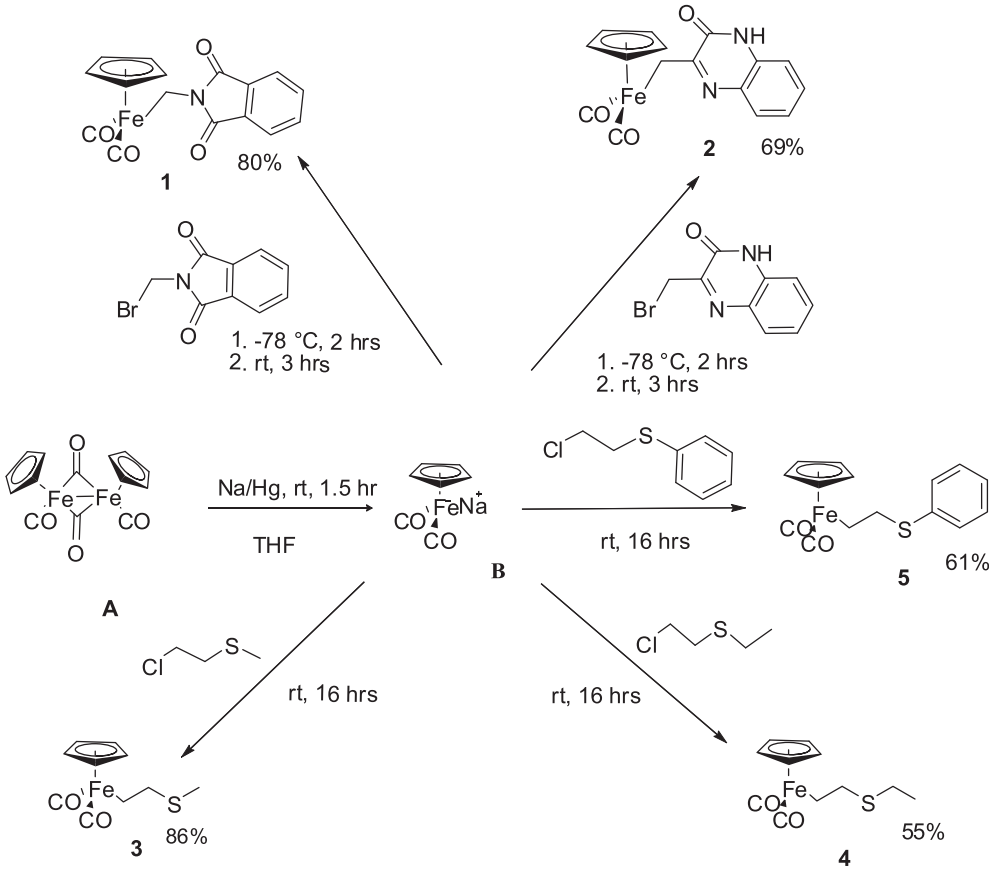
Our current focus is on the use of iron(II) piano-stool complexes as catalysts for the synthesis of CNTs and other SCNMs. An initial report from Mohlala et al. has described the synthesis of pristine multi-walled CNTs by using iron(II) piano-stools [29]. However, we are now introducing more variable heteroatoms within the catalyst and exploring the kind and properties of SCNMs obtained at different conditions.

In this study we report the synthesis of five iron(II) piano-stool complexes and their use as catalysts for the synthesis of SCNMs *via* the CVD method. The first two compounds possess ligands functionalized by nitrogen and oxygen heteroatoms with different structures and amounts of nitrogen and oxygen. Hence, it would be interesting to investigate how these two iron(II) piano-stool complexes will affect the level of nitrogen-doping in the resulting SCNMs. The other three compounds contain the sulfur-heteroatom incorporated in different chain lengths as ligands. These are also explored to establish how the presence of sulfur and varying the ligand chain length affects the yields, morphology and selectivity towards the SCNMs produced.

Results and discussion

Synthesis of iron(II) piano-stool complexes

The synthesis of iron(II) piano-stool complexes proceeded *via* a relatively simple procedure (Scheme 1). This involved reduction of the dimer (compound **A**) with a dilute amalgam (sodium and mercury in THF) at room temperature to form the cyclopentadienyl dicarbonyl iron anion or cyclopentadienyl dicarbonyl metalate (Compound **B**). The nucleophilic anion was reacted *in situ* with the desired electrophile in which the various reactions proceeded *via* a nucleophilic substitution reaction. The reactions involved initial



Scheme 1. Synthesis of iron(II) piano-stool complexes used as catalysts for the synthesis of SCNMs.