Dinuclear transition metal complexes in carbon nanostructured materials synthesis

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Abstract. Carbon nanomaterials (CNMs) were prepared with two similar techniques using organometallic complexes as catalysts precursors. Chemical vapour deposition (CVD) and pyrolysis with chlorine gas approaches were employed in order to explore the effect of dinuclear transition metal compounds \([\text{Fe}_2(\text{CO})_6(\mu-\text{S}_2\text{C}_6\text{H}_2\text{X}_2), \text{X}=\text{OH}, \text{Cl}] \) in synthesis of CNMs. Our to-date results have shown these complexes generate different carbonaceous materials when they are used in bulk, it was also observed that their performances in synthesis differ even though these compounds are analogous. With \(\text{X}=\text{OH} \) complex used in CVD process, metal nanoparticles of ca. 20-50 nm in size and embedded in carbon matrix were obtained. \(\text{X}=\text{Cl} \) complex has been used in pyrolysis experiments and showed an entire volatilisation or no reaction, depending on selected temperature. Furthermore, obtaining of a new tetranuclear iron cluster is presented in this work.

1. Introduction

Nanochemistry devotes with synthetic aspects of the chemistry concerning the production and characterization of materials at the nanoscale [1]. Among the wide spectrum of those, carbon nanomaterials (CNMs) which include carbon nanotubes (CNTs), nanofibres, hollow and filled spheres, etc [2] are generally produced from catalytic decomposition of hydrocarbon gases over selected metal nanoparticles. In this sense, since the growing use of organometallic complexes in synthesis of CNTs as precursor catalysts [3], many studies have recently been done. Most of the study cases present the utilisation of simple organometallic compounds such as ferrocene or \(\text{Fe(CO)}_5 \), however study of ligand effects on CNM synthesis has not been emphasized [2].

Current literature points out that chemical vapour deposition (CVD) technique is the most common used approach to make CNMs due to its capacity to generate various types of nanostructures in a controlled manner and at high yield [4, 5]. A similar approach which involves the chlorination of organometallic compounds has also been explored as an alternative to synthesize CNMs [6].
Organometallic complexes generally undergo decomposition or pyrolysis reactions which make them suitable for the above mentioned methods. Also, they offer in a single molecule carbon source for the creation of carbon structures by means of the ligands, metal atoms for nanoparticle metal catalyst, and other atomic species or functional groups which could play different roles according to their nature.

In this sense, we explored the performance of dinuclear organometallic complexes and the effect of their ligands in synthesis of CNMs by using two different techniques.

2. Experimental Procedure

Organometallic complexes [Fe₂(CO)₆(μ-S₂C₆H₄X₂)], (X=OH, Cl) were synthesised using Schlenk techniques under Ar atmosphere. Compounds 1, Fe₂(CO)₆(μ-S₂C₆H₄OH) and 2, Fe₂(CO)₆(μ-S₂C₆H₄Cl₂), were prepared based on literature procedures [7, 8], respectively. However, while purifying the latter, in a subsequent elution with a mixture of n-hexane/CH₂Cl₂ (10:1) a new compound was unexpectedly isolated, 3, in a 1:10 ratio respect to compound 2, as a dark brown solid. IR (n-hexane) νC=O/cm⁻¹: 2077(s), 2054(vs), 2022(m), 1505(s), 1977(s); νC=C, aromatic/cm⁻¹: 1654(m). ¹H-RMN (CDCl₃, 300 MHz, 22°C) δppm: 7.10 (s, 4H, C-H). MS (FAB⁺) m/z: 781.5-669.5 [M⁺ - nCO; n=5-9]. Elemental Analysis: Calculated to C₂₀H₆S₂Cl₂Fe₂O₈ (Found): C, 26.53 (26.65); H, 0.64 (0.76); S, 13.50 (13.96).

CVD experiments consistent of two steps were carried out using a horizontal CVD reactor: Catalyst precursor preparation and CNMs growth. First, thermal degradation of compound 1 (0.02 mmol) was performed by placing it in bulk on a quartz vial and heated in air at 1073.15 K for 15 min in the CVD oven. Second, thermal CVD synthesis of CNMs was performed under a constant flow pressure by flowing a mixture of H₂ (1500 sccm) and of Ar (200 sccm) currents at 1073.15 K for 20 min to ensure reduction of iron. Subsequently, conditions were readjusted by keeping constant the H₂ and Ar flows and adding to this mixture a flow of ethylene (2 sccm) for 5 min. Finally, the H₂ flow was reduced 100 sccm every 5 min until a final flow of 200 sccm was reached while maintaining the Ar and ethylene flows. Then reactor and products were cooled down to room temperature before microscopy analysis.

Pyrolysis experiments consisted in chlorination of compound 2 (0.02 mmol), placed in a 6 cm long quartz boat, by treatment with a flow of ultrapure Cl₂ gas in a tubular furnace. The samples were heated at two different temperatures and heating ramps (1173.15 K, 50 K/min and 473.15 K, 10 K/min, respectively) during 30 min under a constant flow pressure by flowing a mixture of Cl₂ (25 cm³/min) and Ar (50 cm³/min). NaOH dissolution was connected at the end of the furnace to eliminate the unreacted Cl₂ and the generated volatile metal chlorides byproducts.

The general morphology of the obtained samples was observed with a Philips CM200 FEG (operated at 120 kV) transmission electronic microscope equipped with an EDAX DX4 spectrometer for XEDS by preparation of ultrasonic dispersions of samples in acetone. One drop of this suspension was deposited over a copper grid covered with a holey carbon film. Compounds 1, 2 and 3 were analysed using Perkin Elmer Spectrum BX FT-IR, Bruker AMX-300 NMR, VG Autospec (Waters) MS using NBA as matrix in FAB⁺ experiments, and LECO CHNS-932 Elemental Analysis.

3. Results and Discussion

Compound 1 used as precursor of CNMs by CVD process led to two types of carbon aggregates: embedding carbon and irregular unshaped carbonaceous material. As shown in figure 1, the sample is composed by metal nanoparticles of spherical shape and size of ca. 20-50 nm, embedded in carbonaceous matrix (a) and most of the irregular carbonaceous material is empty. XEDS analysis of metal particle marked with the arrow showed that it is composed of Fe, although traces of C and O is detected too, and is correspondent to the axis zone [001] of α-Fe phase (b). A magnification of the area marked with the circle is shown in (c), and we can see that spherical iron nanoparticles are encapsulated by an amorphous carbon wall and which seem to be composed of some carbonaceous layers. Moreover, the same experiment carried out in absence of ethylene only gave a rusty powder with no carbon content which would indicate that organic part of 1 is not a significant carbon source.
These results are in contrast with our previous studies [9] employing 1 in CVD process by using the same experimental conditions but with 1 previously deposited in silica substrates instead of in bulk. When deposited, nanoparticles generated by 1 are homogeneously distributed in the substrate surface which promotes a uniform catalytic activity in the CNTs growth. According to our results reported here they could be explained by the smaller number of active sites when precursor is treated in bulk, which would lead to the formation of nanoparticles with an irregular packing and subsequently, they could not be enough to achieve the growth of carbon nanotubes. In this case, if we consider the carbon from the ligands as an impurity, then it could be explained the presence of metal nanoparticles surrounded by carbon. Although it seems that the presence of oxygen could take an unusual role in its reaction performance by poisoning the iron catalyst [10] the presence of sulphur near the iron atoms could play a more significant role in the formation of carbon nanomaterials [11].

Attempts to obtain CNMs by using 2 through pyrolysis experiments failed under the used experimental conditions. When performed with the common temperature used in this type of experiments, 1173.15 K, we observed an entire volatilisation of precursors and no type of carbon soot. It is possible that in addition to the expected FeCl$_3$ byproduct, also another kind of chlorination process would be consuming the carbonyl and aromatic moieties, may be in the form of CCl$_4$ [12]. In contrast, at a temperature of 473.15 K there was not reaction, which could be attributed to the molecular weight of precursor as compared when organometallic complexes are mononuclear [6]. Both results suggest that the formation of CNMs would be achieved in temperatures between the tried ones, more likely near the 1173.15 K. New experiments are currently in process.

Characterisation of the unexpectedly obtained compound 3 indicated that is a tetratetranuclear iron cluster likely with a tetrahedral geometry containing nine terminal carbonyl groups surrounding the
core atoms and two disulphide ligands between each two metal centres, bearing one aromatic ring each one. IR spectrum showed a different and complex pattern in the carbonyl region as compared to the parent and to the related compound 1 and it might be as a consequence of the asymmetrical distribution of the nine carbonyl groups. \(^1\)HNMR spectrum showed one singlet correspondent to the four protons of the two aromatic rings. Elemental analysis suggests the molecular formula \(\text{Fe}_4(\text{CO})_9(\mu-S_2\text{C}_6\text{H}_2\text{Cl})_2\) and MS FAB\(^+\) experiments indicate the sequential loss of carbonyl ligands in addition to concordant theoretical and experimental isotopic distributions [13]. Essays to obtain a crystal are in process to determine its structure. This complex 3 which has a structure that resembles the compound 2, but doubled itself, could be employed in pyrolysis experiments and it is possible that might lead to CNM structures mainly due to the higher metal nuclearity and molecular mass of the cluster which could avoid the previous volatilisation problems, and furthermore, it is also possible that due to the odd number of carbonyl ligands its reactivity towards the chlorination process will be favoured. Preparation of these experiments is currently in process.

4. Conclusion
Analogue organometallic complexes containing metal centres, disulphide and carbonyl ligands, and an aromatic ring, were employed in synthesis of CNMs using two different approaches. The first compound was employed in bulk in CVD process and gave spherical metal nanoparticles of 20-50 nm in size surrounded by carbon matrix, and amorphous carbonaceous material. Using organometallic precursor in bulk showed very different performance as compared when deposited in silica, which suggests a searching for a further alternative substrate or a simpler deposition method. Second complex also used in bulk and pyrolysed at two different temperatures led to two extreme results in the chlorination process: at the higher temperature the precursor underwent an entire volatilisation, and at the lower one there was no reaction. In spite of this, it is possible that running experiments at intermediate temperatures might lead to CNMs, which are dependent of many variables. Moreover, a new compound was obtained and characterised, and it seems to be suitable as CNMs precursor.

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