Growth of carbon nanotubes from supported metal catalysts

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Abstract

The growth of carbon nanotubes (CNTs) from supported metal catalysts is under investigation using the chemical vapour deposition (CVD) method with CH₄ as the carbon feedstock. Studies include the effects of the structure of the support media, metal catalyst content and other experimental parameters on the CNTs produced. The effects of the surface structure on the catalyst particles and the CNTs produced are being investigated using various alumina-based supported iron catalysts. Supported catalysts have been prepared from ferric sulphate and either aluminium nitrate or delta-alumina nanoparticles in order to produce different substrate morphologies. Preliminary TEM studies indicate that under the same experimental conditions Fe supported on alumina nanoparticles produces mostly bundles of DWCNTs, whereas Fe supported on alumina derived from aluminium nitrate produces predominantly SWCNT bundles with some MWCNTs. The effects of catalyst content on the CNT production is also being investigated with Fe content varying between 5% and 30%. Preliminary TEM results show the presence of bundles of SWCNTs for all the Fe contents except 5% Fe; no CNTs have been observed in this sample.

Introduction

Carbon nanotubes have generated a great deal of interest since their discovery [1] due to their unique structural, electronic and mechanical properties leading to potential applications of SWCNTs in the microelectronics industry [2-5]. Effective catalysts for growing CNTs using the CVD method are transition metals, their oxides and their mixtures supported on a substrate. The interactions of the substrate with the catalyst need to be understood as they influence the metal catalyst particles formed on the surface which in turn catalyses CNT formation. In order to increase the yield of CNTs produced the surface area of the substrate needs to be as high as possible and as a result aerogels are also increasingly being investigated [6-9]. The focus for this research is to investigate the formation of SWCNTs by exploring the roles of the support medium and the catalyst.
Experimental Method

Catalyst Preparation

Supported catalysts have been prepared from ferric sulphate and either aluminium nitrate or delta-alumina obtained from Degussa, in order to produce different substrate morphologies. Two $\text{Al}_2\text{O}_3$-Fe catalyst aerogels were prepared using the same starting materials (aluminium nitrate and ferric sulphate) and ratios but different drying conditions. 0.1M aluminium nitrate was dissolved in 70ml saturated ethanol solution of ferric sulphate and then either dried normally to produce aerogel 1, or super-critically dried at 7.5MPa and 260°C, for 30 minutes to produce aerogel 2. The third catalyst (3) was prepared from the same starting materials as the aerogels, but with different Fe concentrations, to investigate the effects of catalyst content on CNT production, with Fe content varying between 5% and 30%. The fourth catalyst (4) was prepared using delta-alumina nanoparticles, with an average particle diameter of 13nm, and ferric sulphate dissolved in ethanol and dried normally. The Fe content in all cases was 20% except where otherwise stated.

CNT growth

The samples were prepared by direct pyrolysis of flowing methane over a silica boat containing the catalyst, for 30 minutes at various synthesis temperatures. The catalyst was heated from room temperature to 800°C in 1hr, and then heated to the required synthesis temperature in 30 minutes, under $\text{N}_2$ atmosphere. The catalyst was then held at the synthesis temperature for 30 minutes under a methane atmosphere. For aerogel 1, the synthesis temperatures investigated were 860°C and 880°C, whereas for aerogel 2, the temperature range was 880°C to 970°C in 20°C increments at a $\text{CH}_4$ flow rate of 250ml/min for both aerogels. Using catalyst 4, the $\text{CH}_4$ flow rate, synthesis temperature and growth time were investigated and these optimum conditions were found to be 3L/min, 880°C, 30 minutes, respectively. These conditions were used for growing CNTs using catalyst 3.

Results

From TEM investigation, both aerogels produced MWCNTs, with aerogel 1 also producing SWCNTs. The CNTs in aerogel 1 were produced at lower temperatures and were of better quality and of higher yield, than the aerogel 2 catalyst grown MWCNTs. For aerogel 1, very little difference was observed between the samples prepared at different synthesis temperature, whereas for aerogel 2, very few MWCNTs were observed at the lower temperatures that appeared to be filled with the substrate; the yield and quality of these MWCNTs was observed to increase with temperature, at 960°C and 970°C, the MWCNTs produced were ’empty’ tubes as in the other samples.

Fig 1 shows CNTs produced for a range of different Fe concentrations. As can be seen from the TEM images, bundles of SWCNTs are produced over a wide range of Fe concentrations. However, for the 5% Fe, no CNTs were observed even though it is expected that some CNTs be present in this sample, at least in small quantities. At very high concentrations, it is expected that fewer SWCNTs will be produced due to the
Fig 1. CNTs produced from catalyst 3 for various Fe concentrations. CNTs were grown at 880°C, at a flow rate of 3L/min for 30 minutes.
a and b) TEM images showing CNTs produced for sample containing 10% Fe,
c and d) TEM images showing CNTs produced for sample containing 15% Fe,
e and f) TEM images showing CNTs produced for sample containing 20% Fe,
g and h) TEM images showing the CNTs produced for sample containing 25% Fe,
i and j) TEM images showing CNTs produced for a sample containing 30% Fe.
agglomeration of iron on the substrate surface to produce large particles that would result in the formation of MWCNTs rather than SWCNTs. It seems reasonable to assume that there will be an optimum Fe concentration at which SWCNT formation is dominant over MWCNT formation, as observed by Peigney et al [10]. However, from TEM observations, it is difficult to determine the changes in SWCNT yield with changes in Fe concentration. Further analysis is being carried out.

CNTs produced from Fe catalyst supported on alumina nanoparticles (catalyst 4) can be seen in Fig 2. A large amount of CNTs were present in this sample including MWCNTs and bundles of SWCNTs with many bundles containing combinations of SWCNTs and DWCNTs as can be seen in fig 2b. Employing the same conditions as for catalyst 3, catalyst 4 produced mostly bundles of DWCNTs whereas catalyst 3 produced largely bundles of SWCNTs, as determined from TEM observations.

![TEM images showing the presence of bundles of tubes (a) consisting of DWCNTs and SWCNTs (b), grown using delta-alumina nanoparticles (catalyst 4), at 880°C, 3L/min for 30 minutes.](image)

**Conclusion**

CNTs produced from aerogel 1 produced better quality and higher yield MWCNTs and bundles of SWCNTs, at lower temperatures, than the supercritically dried aerogel catalyst. For aerogel 1, very little difference was observed between the SWCNTs and MWCNTs produced at different synthesis temperature whereas for aerogel 2, the quality and yield of CNTs was observed to increase with temperature. Preliminary TEM results show the presence of bundles of SWCNTs for all the Fe contents except 5% Fe; no CNTs have been observed in this sample.

Using aluminium nitrate, bundles of good quality SWCNTs were produced, however, when using the delta-alumina nanoparticles, bundles of MWCNTs were observed containing mostly 2 walls, under the same experimental conditions. Surface area
analysis and further TEM analysis of the support medium and the catalyst is underway. Further surface morphology effects will be investigated using gibbsite calcined at different temperatures in order to produce different surface structures with a view to realising the correlation between the supported catalyst and SWNCT formation.

References