Synthesis of carbon nanotubes on alumina-based supports with different gas flow rates by CCVD method

R Aghababazadeh, A R Mirhabibi, H Ghanbari, K Chizari, R M Brydson and A P Brown

1 Iran Colour Research Centre, No.32, Afshari Street, Hemmat Highway Junction, Tehran, Iran
2 Materials and Metallurgy Department, Iran University of Science and Technology, Hengam Street, Narmak, Tehran, Iran
3 Institute for Materials Research, University of Leeds, Leeds, LS2 9JT, UK

Email: r_babazadeh@yahoo.com

Abstract. Several methods for the synthesis of carbon nanotubes have been developed in the last decade. The CVD process and their associated parameters affect the structure of the resulting nanotubes. In this work CNT growth has been studied on different supported catalysts with different rates of gas flow as one of the critical points. Different supports were prepared by mixing nanosized alumina with tetraethyl orthosilicate (TEOS) by a chemical method at low temperature and iron as the metal catalyst was impregnated by 5%, 10% and 20% weight of the supports. Methane was used as a carbon source for the synthesis of CNTs at 800°C-1000°C. Aluminium-based support, supported catalysts and CNT samples have been characterised by TEM, SEM, BET and XRD.

1. Introduction
Carbon nanotubes (CNTs) are a new class of materials, containing of small tubules formed by rolling graphitic sheets discovered by Iijima in 1991 [1, 2]. These novel materials have been extensively investigated in the past few years because of their unique structure, excellent mechanical properties and promising electronic characteristics and so are predicted to have great future potential in science and industrial applications [3].

Production of nanotubes has been experienced by various methods. The Catalytic Chemical Vapor Deposition (CCVD) technique appears to be a promising method for utilization on the industrial scale since it leads to large yields of carbon nanotubes at low cost of production compared to other synthesis methods such as Arc-Discharge and Laser Vaporisation [4,5,6]. SWNT growth by the CCVD method is affected by the catalyst (composition, type of support and nature of the metal), and carbon source [6].

2. Experimental

2.1. Support Preparation
For preparing S1 supports, nanoparticles of Alumina (γ-δ from Degussa) was suspended in ethanol. Then TEOS (Tetraethyl Orthosilicate, C8H20O4Si, Merck) was added to the suspension and stirred for
15 min. After hydrolysing the TEOS with DI water, HNO₃ was introduced to the mixture. After stirring the mixture it was heated under 90°C, dried and ground in mortar agate and passed through a 400 mesh sieve to remove coarse aggregates. The molar ratios of the compounds TEOS: Al₂O₃: HNO₃: H₂O: Ethanol =1: 1: 1.38: 27.76: 85.74.

2.2. Catalyst Preparation
Catalysts were made by introducing Fe₂SO₄.5H₂O (Aldrich, 97%) with 5%, 10% and 20% weight of S₁ to the support.

For impregnating the supports with iron, Fe₂SO₄.5H₂O was added to the S₁ which had been suspended in water. The mixture was stirred for 15 min and heated at 90°C for 2h. The dried powder was ground in an agate mortar and passed through a 400 mesh sieve to remove coarse aggregates. The molar ratios were Fe: Al₂O₃:SiO₂ = 1:16:16.

2.3. CNT Production
Production of CNTs was carried out in a horizontal flow furnace at 900°C in nitrogen atmosphere (99.999% purity) by the catalytic reaction of methane (99.99% purity) on an as-prepared catalyst in a fixed bed reactor. After passing nitrogen, methane was passed over the catalyst bed for 30 min with a flow rate of 4, 6 and 8 l/min and again nitrogen was passed over the reacted catalysts in the considered flow rate until cooling of the furnace to room temperature.

2.4. Characterisation
The supports, supported catalysts and grown CNTs were investigated by Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and X-Ray Diffraction (XRD). Also the surface area and densities of the samples were measured.

3. Results and Discussion

3.1. Support characterisation
An XRD pattern of the support showed that a hybrid of Alumina and silica was formed by this method. The study of the pore structure of the support (S₁:Al₂O₃-SiO₂) by the BET method with N₂ shows a mixture of type I and IV of characteristic adsorption isotherms (Figure 1). The knee shape of the graph at low p/p° indicates small amount of micropores and the hysteresis indicates the existence of mesopores [9]. The surface area of the support by the BET method was determined to be about 351.6 m²/g. Average pore diameter is 52.8Å. The support density and surface area are shown in Table 1. These results are rather complicated to be judged by the BET data, therefore it seems further studies need to be followed for clarification of these results.

| Density (g/cm³) | S₁ | S₁C₅ | S₁C₁₀ | S₁C₂₀ | S₁C₁₀NTF₆ | S₁C₁₀NTF₈ |
|----------------|----|------|-------|-------|------------|------------|
| Surface area (m²/g) | 351.6 | 2.50 | 2.50 | 2.51 | 57.9 | 63.3 |

F stand for flow rate and the subscript shows the rate in l/min. C stand for concentration of the catalyst and the corresponding subscript shows the weight%. NT stand for the prepared nano tube.

3.2. Supported catalyst characterisation
An XRD pattern of the supported catalyst shows the presence of Fe₂O₃ besides the alumina and silica. The surface area of the sample with 10% weight of iron (S₁C₁₀) was 21.7 (m²/g). The densities of the catalysts are shown in Table 1.

| Table 1. Densities and surface areas of supports, catalysts and nanotubes | S₁ | S₁C₅ | S₁C₁₀ | S₁C₂₀ | S₁C₁₀NTF₆ | S₁C₁₀NTF₈ |
|----------------|----|------|-------|-------|------------|------------|
| Density (g/cm³) | 2.44 | 2.50 | 2.50 | 2.51 | – | – |
| Surface area (m²/g) | 351.6 | 21.7 | – | 57.9 | 63.3 | – |
SEM micrographs of the samples with 10% (S1C10) and 20% weight of iron (S1C20) are shown in figure 2. As can be seen these catalysts are not homogenised catalysts but EDX from different parts of the samples showing the presence of iron element on the support.

3.3. Nanotube characterisation

Figure 3 shows the SEM pictures of the as-synthesised carbon material. SEM pictures of carbon filaments which are grown on the catalysts with 10% weight of iron at flow rates of 4, 6 and 8 l/min (S1C10NTF4) (S1C10NTF6) (S1C10NTF8) and 20% weight of iron at flow rates of 4 and 6 l/min (S1C20NTF4) (S1C20NTF6) are shown in figure 3. It can be seen that the grown nanotubes on the S1C10 catalysts at different gas flow rate are longer than on the S1C20 catalysts. No filaments were seen on the S1C20 at a flow rate of 8 l/min.

The TEM images of the supported catalyst with 5% and 10% weight of iron subjected to methane treatment are shown in Fig. 4. These figures revealed that the carbon filaments in SEM images are
nanotubes. Also amorphous carbon can be detected on the walls of the tubes. Figure 4.c shows the mapping of iron enclosed by nanotubes (white regions).

A comparison of the TEM images of the multiwall nanotubes which are grown on impregnated support by 5% and 10% weight of iron with the same flow rate of methane indicated that the nanotubes on the second catalyst (S,C<sub>20</sub>NT) are thicker than the first group of synthesised nanotubes (S,C<sub>10</sub>NT).

Surface areas of the samples are shown in Table 1. Surface area data revealed that an increase of the rate of gas flow increases the yield of production.

![Figure 4. TEM pictures of the Nanotubes in (a) S,C<sub>5</sub>NTF<sub>6</sub>, (b) S,C<sub>10</sub>NTF<sub>6</sub> and (c) mapping of iron as a seed of the nanotubes in S,C<sub>10</sub>NTF<sub>6</sub>](image)

4. Conclusions
Because of the less time of contact between the gas and catalyst the decrease of nanotube growth can occur due to decreasing of flow rate of methane. By increasing the amounts of iron the number of walls of tubes increases and the length of tubes decreases.

5. References
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