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Effect of Molecular Interaction Towards Homogenous Diameters for Synthesized MWCNTs from Methanol/Butanol mixture by CVDs

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Abstract:

Carbon nanotubes with multi-wall (MWCNT's) with homogenous diameters were successfully synthesized from (1:1) Methanol/Butanol by chemical vapor deposition (CVD) at 700°C using Fe as a catalyst. The mixture of alcohol includes low ratios of amorphous carbon with high ratios of carbon atoms which are able to covert for MWCNTs. The product was characterized by XRD, Raman spectroscopy, SEM and EDX analysis shows the formation of carbon nanotubes MWCNT's. The diameter of tubes shows semi-equal value when arrange between 90-105nm and the homogeneous length reached to more than 8µm. The molecular interaction for the mixture of C1\C4 alcohol plays an important role towards the reduction and changing the skeleton of the agglomerations for the molecules at vapor phase.

Keywords: Molecular Interaction, Butanol, Methanol, CVDs, Clusters

1. Introduction:

Synthesis of nanomaterials (NMs) with homogenous quality and quantities considered as a big challenge for the scientific institutes.. NMs such Carbon nanotubes CNTs increase the needed to synthesize more quantities with specific properties to make it suitable for potential applications [1]. CNTs were characterized with internal, external diameters and the length which could control by the preparing conditions [2] and synthesizing methods such as arc discharge, laser ablation and chemical vapor deposition CVD. The types of catalyst or temperature of precipitation and the technic of synthesis process were commonly used to limit the types of CNTs. The molecular structure of the precursor could influence directly the structure of carbon nanotubes. The high number of carbon atoms (more than seven atoms) are used to form branching CNTs [3], while cyclic hydrocarbons such as benzene [4] are

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used to produce curved CNTs. Generally linear hydrocarbons like methane and ethylene t decomposed thermally to produce hollow CNTs.

Mixture of alcohol (for example, ethanol/methanol mixture) [5] as the carbon source, formed few walled CNTs with high purity. Methanol represent the typical sources for synthesized CNTs maybe the less by product or the OH radical, which evolves from its dissociation [6] which enhance the growth. In this work MWCNTs were prepared with homogenous length and diameter from 50/50 mixture of methanol and butanol C1/C4 on the support cover with ferrocene as a catalyst for the growth. The process carry out at atmospheric pressure and 700°C . The growth depends on the molecular interaction for C1 and C4 alcohol towards homogenous evaporation than ideal decomposition for semi-equal diameter tubes.

2. Experimental

2.1 Materials

Methanol, Ethanol and Butan-1-ol with purity of 99.93%, 99% and 99% , respectively, were purchased from Alfa Assar. Hydrogen peroxide H2O2 was purchased from Spain 30% percent weight for purification process. N2 gas, which is used as a carrier gas, was brought from the UAE with purities of 99.99%. Ferrocene were purchased from Sigma.

2.2 Synthesis of CNTs

The multi–wall carbon nanotubes MWCNT's were prepared by chemical vapor deposition CVDs, which is done by tube furnace with three stages from Nabertherm USA. The tube furnace consists of quartz tube with 120 cm in length and 5 cm in diameter. Ceramic boat was used as a support for catalyst of precipitation which includes a 200 mg of ferrocene. Before switching on the tube furnace, nitrogen gas was purged to remove the air from all the tube reaction with flow rate 125 cm3/min. The furnace was switched on and heated to the reaction temperature at 700 ºC with flow rate of heating 3.4°C/min at atmospheric pressure, and a typical reaction time 30 min in a nitrogen atmosphere and a flow of 125 cm3/min. When the furnace reached the desired temperature, the N2 gas flow was reduced slowly to the rate of 80 cm3/min. The N2 gas carried the sources of carbon when passed through a vaporizer the mixture (1:1) C1/C4 which evaporate at 70ºC. After deposition, the furnace was switched off and allowed to cool down to the room temperature under a continuous N_2.

3. Result and discussion:

X-ray diffraction (XRD) was done by Riga Rota flex / RU-200B, the Sentara infinity 1 Broker used for identified Raman spectroscopy. Scanning electron microscopy SEM and Energy-dispersive X-ray spectroscopy EDX observations are used (a JEOL JSM--6700F) to characterize the purified CNTs. Fig. 1 shows the XRD results for the as-grown carbon nanotubes with strong and sharp diffraction around 2θ = 25.9° could be related to C (001) reflection of graphite. The second week and wide peaks at 43.8° may attribut to the lattice plane of C structure (002) [6]. The peaks at 36°, 55O, 58 O and 64° could be related to the Fe which is used as a catalyst and may interference the synthesized CNTs [8].

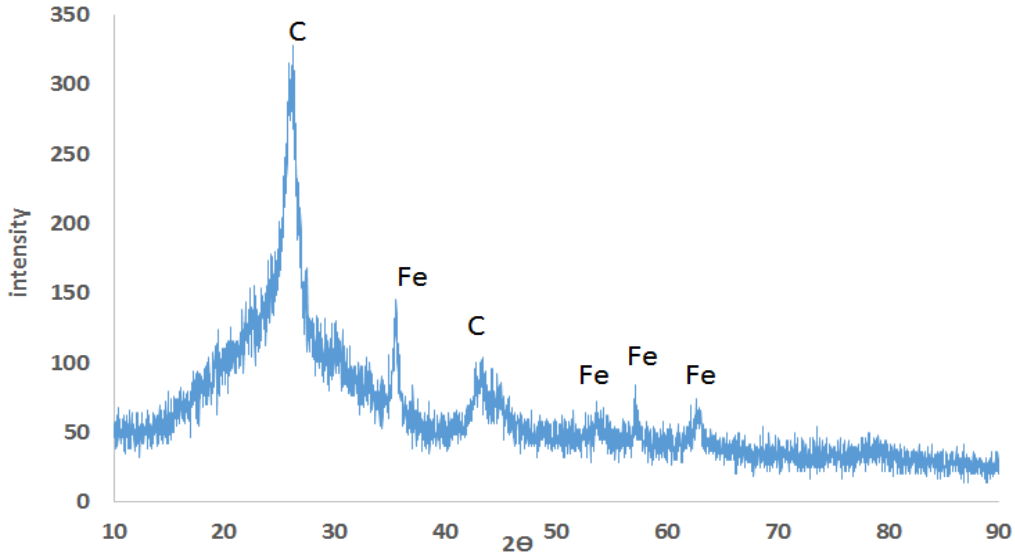

Figure 1. XRD patterns of the MWCNTs obtained at 700ºC on the ferrocene as catalyst from 50/50 (v/v) C1:C4 in N_2 atmosphere.

Raman spectroscopy was shown in Fig. 2. it includes two peaks that could be attributed to D and G lines at 1359 and 1578 cm¹, respectively while a weak peak appeared at 2937 cm^{-1} is assigned to the G+D. The peaks refer to MWCNTs with good crystalline quality and less distortion due to the ratio intensities of I_D/I_G was equal to 1.39 which may relate to typical temperature of precipitation [9].

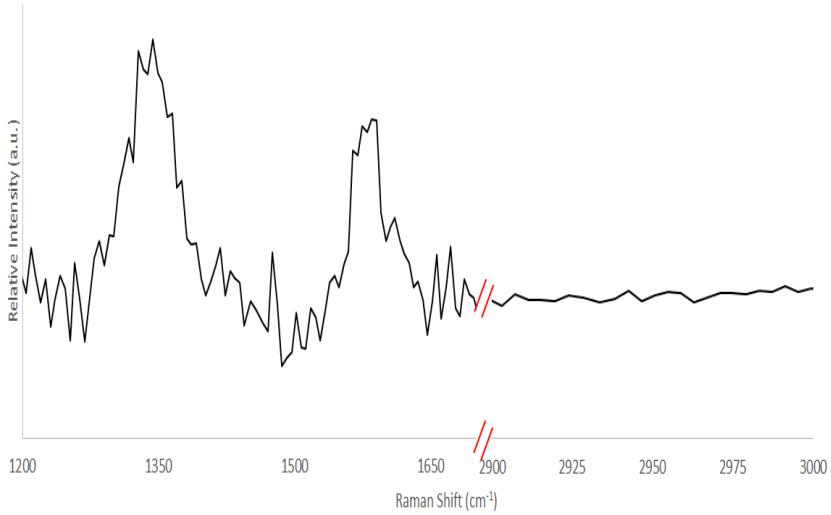

Figure 2. Raman spectra of MWCNTs obtained at 700ºC on the ferrocene as catalyst from 50/50 (v/v) C1:C4 in N_2 atmosphere.

The SEM images of the MWCNTs obtained from the chemical vapor deposition for 1:1 of C1:C4 alcohol at 700 ºC in N2 atmosphere are shown in Figure 3. MWCNTs with more than 8 μm in length represents the growth rate of 0.3 μm min−1. The diameter of tubes shows semi-equal value when arrange between 90-105nm for most the MWCNTs as plotted in Figure 4 with 200 nm in scope. The SEM images also show that the MWCNT s observed at several places, which attached to the surfaces of some unconverted carbon mostly refer to amorphous carbon.

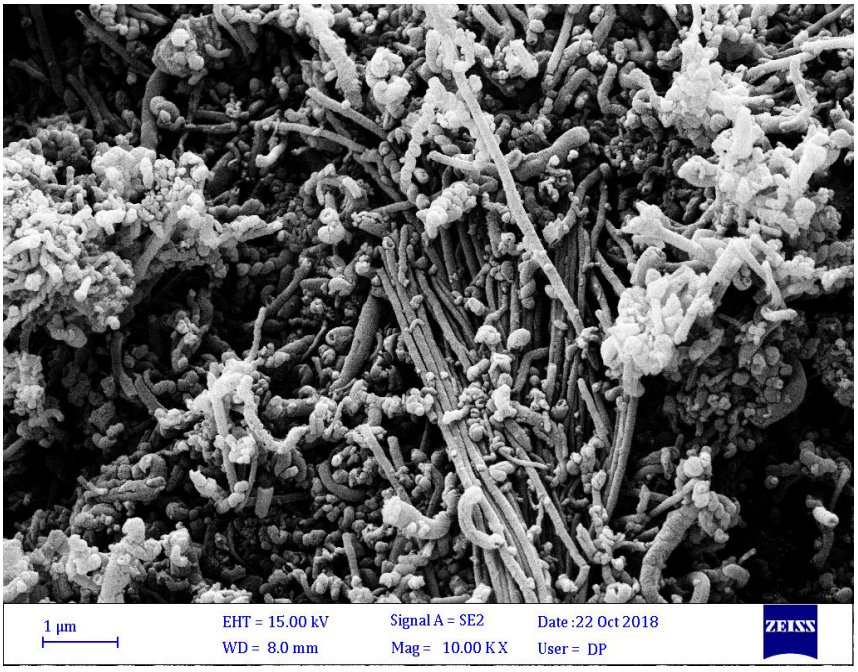

Figure 3. SEM image at 1µm diameter for synthesized MWCNTs deposited from C1:C4 at 700 ºC catalyzed on the ferrocene surface.

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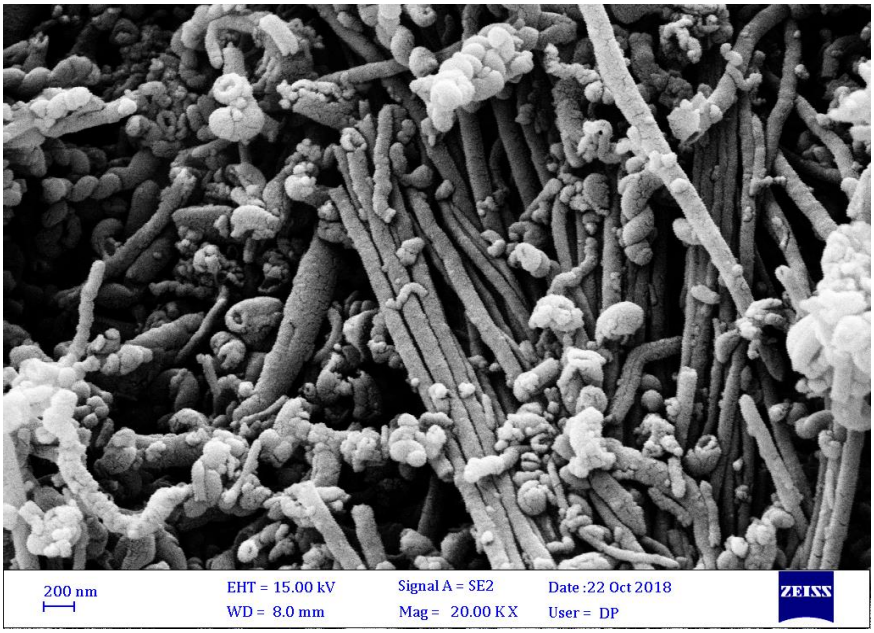

Figure 4. SEM image at 200 nm diameter for synthesized MWCNTs deposited from C1:C4 at 700 ºC catalyzed on the ferrocene surface.

Energy dispersive X-ray spectrometry (EDS) analysis shows the presence of iron nanoparticles, which is used as catalyst for precipitation of CNTs on the support surface. Ferrocene is employed as a catalyst to promote the formation of graphene sheets, to conform CNTs walls during the synthesis process. The trice element Mo, Mg and S with Au represent the remaining materials for the support surface which may not remove during the purification process.

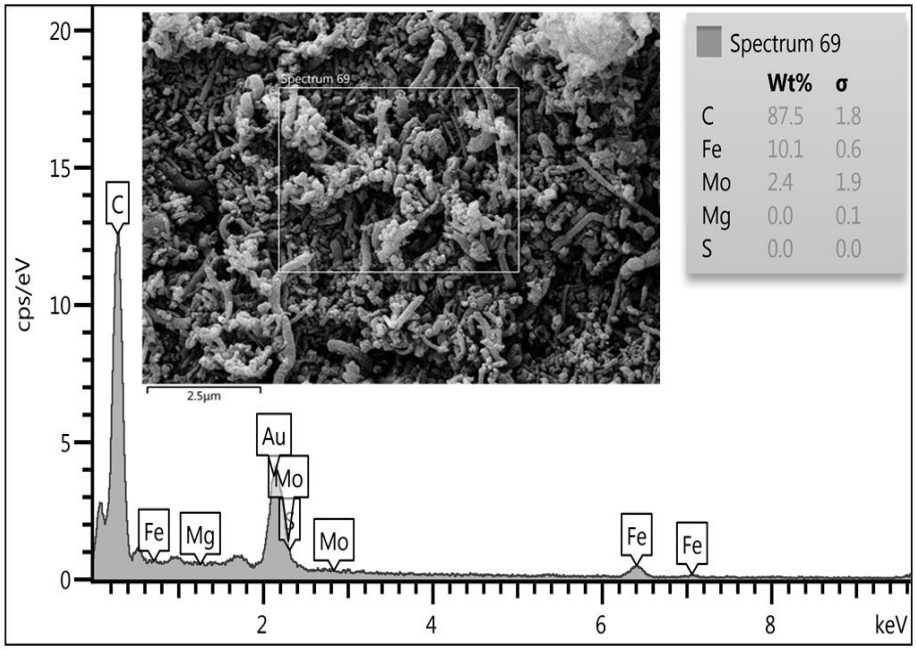

Figure 5. SEM-EDX analysis represents the dispersion of Fe and trace element Mo, Mg, S, and C in the synthesized MWCNTs in N2 atmosphere.

The boiling point of C1 and C4 is 64.7^{o} and 117.7^{o} respectively, when preparing mixture with 1:1 ratio the temperate was fixed at 70° as reported in experimental section. The nature of functional groups for the binary mixture play important roles in create ideal interference towards real connections between C1 and C4 alcohol for less size of cluster then less boiling point **[**10**]**. The energy of the mixed straight line or homogenous is larger than that resulting from the sum of contributions from the heterogeneous or non -linear mixture. Experimentally and theoretically the largest deviation from the ideality was observed for clusters with the equimolar composition which is clearly seen for even-numbered clusters [11]. Hence, we have the theoretical confirmation of the results obtained from the excess absorption spectra. The modeling combustion **[** 12 **]** results of hydrocarbons mixture, mostly for different physical mixing qualities causes variance in reactivity towards dissociation and forming product. The reasons which mentions before confirm that the miserable mixture convert to homogenous mixture with increase temperature causing more interference for C1 when exist in linear chain towards C4. The interference responsible for observed clusters with the equimolar composition between C1 and C4 as shown in figure 6.

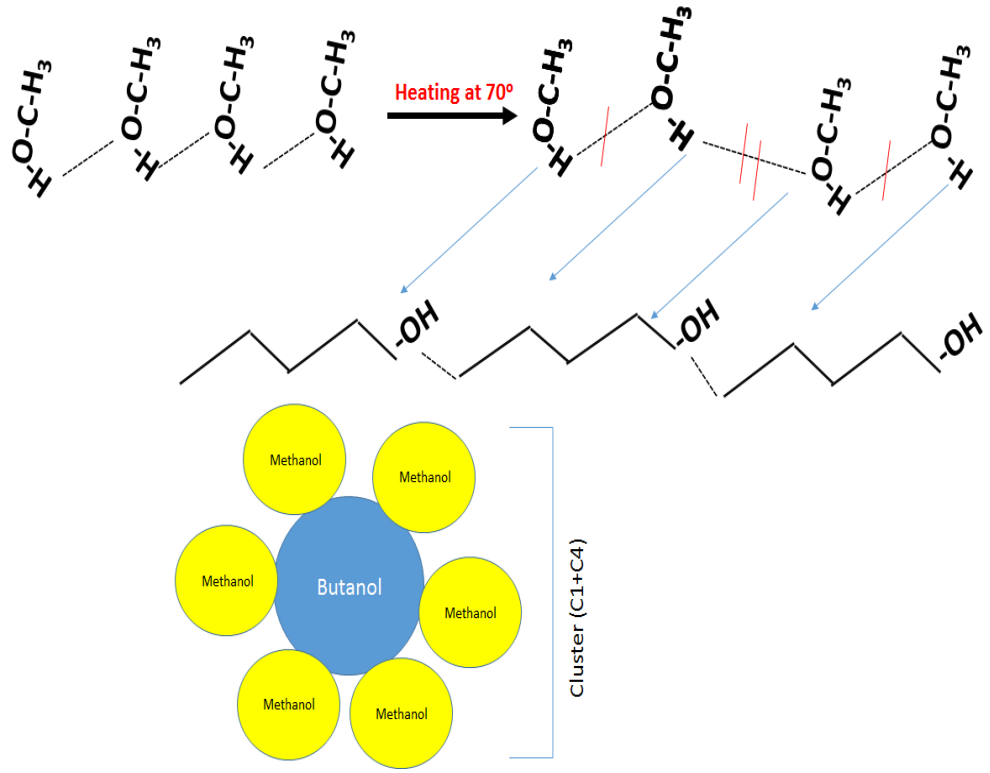

Figure 6: The proposed mechanism for forming cluster of Methanol/ Butanol (C1/C4)

The mixing of two alcohol one with low boiling point C1 and the other with high boiling point C4 at the same ratios mostly caused a reduction in the boiling point for the mixture with new orientation for the molecules [13]. The change of orientations causing new benefit towards change agglomerations like clusters for the molecules which causing modified behavior for the cluster to degradation then precipitation with forming tubular structure.

Conclusion:

The best conditions for growing CNTs can be controlled by many factors: the types of substrate and the nature of mature with composite. Carbon nanotubes with homogenous diameters were synthesized by CVDs method at 700°C at N2 atmosphere using equal volumes of methanol and butanol. The molecular interaction plays critical roles towards control the process of precipitation when create new orientations for the alcohol molecules. The benefit of mixing is reducing the temperature of boiling with increasing the evaporation of mixture and producing less quantities of amorphous carbon. The quality of the samples analyzed by XRD, Raman spectroscopy and

SEM with EDX reveal that equal ratios of C1 and C4 are ideal responsible for nature of product.

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