Exploring the Mechanism of Nanotube Formation

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Carbon nanotubes (CNT) have attracted vast interest due to their excellent mechanical, physical, chemical and electronic properties and due to their high potential for future applications. Although many different production methods have been proposed since 1991 graphite arc discharge, laser ablation and chemical vapour deposition (CVD) techniques can be considered to be the most common ones. Arc discharge and laser vaporization techniques are considered to be the high temperature routes since the temperature can reach to 5000 and 10000 K respectively. On the other hand CVD and its variations are classified to be the medium temperature methods. Reaction temperature in CVD methods ranges between 550 ºC and 1200 ºC. Researchers currently work on to reduce the growth temperature of CNTs in order to make it applicable for electronics industry and to make it suitable for many substrate materials. Despite the fact that numerous catalyst materials, many different catalyst preparation techniques and various carbon feedstocks have been tried out, the mechanism involved in growing CNTs remain poorly understood. Researchers from catalyst community mainly study the growth rates as a function of various parameters however material scientists are mostly interested in the properties of the final product.

For high temperature routes gas, liquid and solid mechanisms have been proposed for multiwalled carbon nanotubes (MWCNT) [1]. According to the gas mechanism smaller carbon fragments combine in the gas phase to form CNTs and condense on cold spots. On the other hand solid mechanism states that nanotubes do not grow in the plasma rather they form on the cathode as a result of solid state transformations. Nucleations of nanotubes within "droplets" of carbon deposited on the cathode forms the basis of the liquid mechanism. The tips of the nanotubes in the cathodic deposits were found to be decorated with beads of amorphous carbon and the appearance of these beads was suggestive of liquid droplets [2]. Single walled carbon nanotubes (SWCNT) do not form in the cathodic deposit but grows on the cold reactor walls. Co-condensation of carbon and metal forms liquid metal carbide particle and when the particle becomes supersaturated, solid phase begin to form.

For CVD similar mechanisms have been proposed to occur in order to grow nanotubes. However there are other steps yet to be explored to understand the growth mechanism. Diffusion of the precursor species to the surface of the metal-carbide particle, adsorption of the species on the surface, surface reaction to form C and other gas phase products, diffusion of the C through the metal-carbide particle, precipitation of C in tubular form out of the catalyst particle, and diffusion of product gases away from the particle. No careful experimentation have been reported to identify the rate controlling step of this scenario. Some reports state that the type of the catalyst is not critical in CNT growth [3]. Rather the reaction temperature and carbon feeding rate are more important. Under a given experimental condition there is an optimal catalyst size. Smaller particles are easily poisoned due to overfeeding and larger particles are inactive due to underfeeding.

In this study we aimed at determining the gas phase concentrations of various species during CNT growth and looking for a relation between the intermediates and products of the reaction and growth and morphologies of CNTs. For this purpose a quartz tubular reactor, fitted with mass flow controllers and a sampling line was online connected to a GC/MS system. Schematic representation of the experimental system is illustrated in Figure 1. Reactant and carrier gases were mixed in thoroughly in a stainless steel wool packed chamber and injected into the reactor through a water cooled probe at a specified location. Moving the

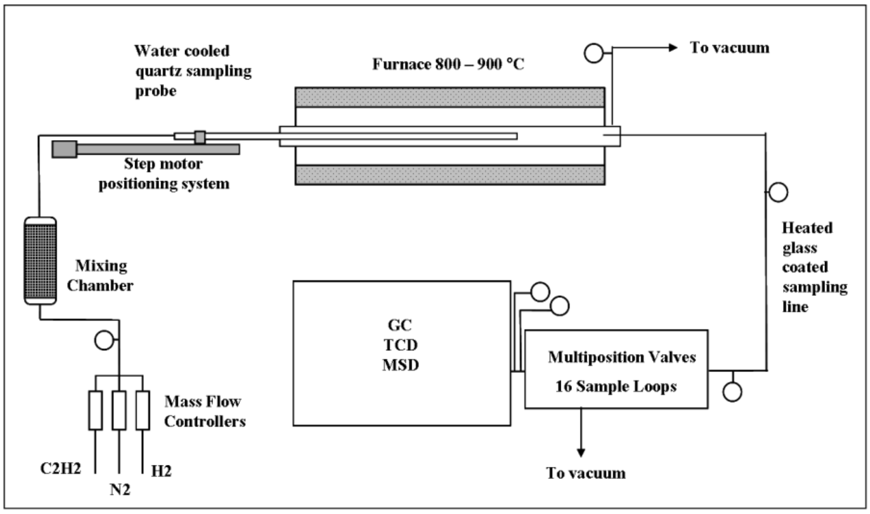
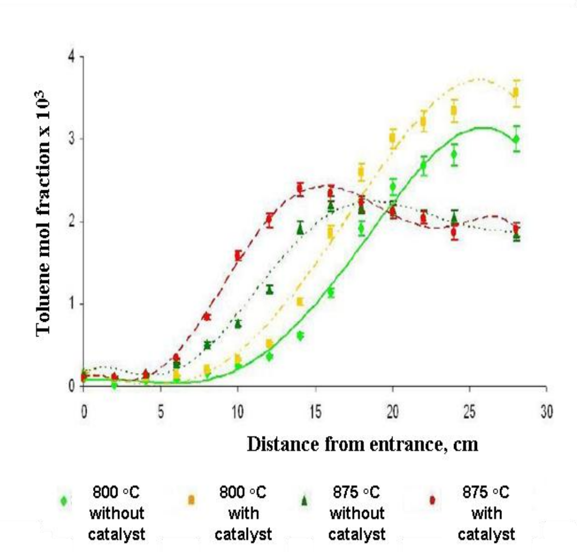
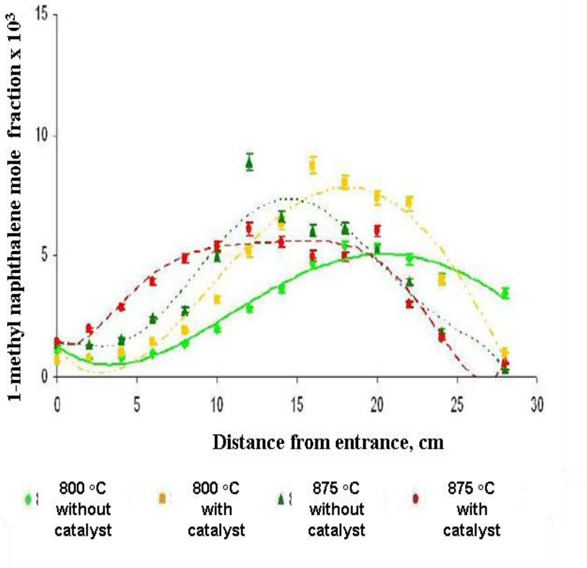


Figure 1. Schematic representation of the experimental system

injection probe in the reactor lets us to study different residence times for the reaction. Exit gases from the reactor were collected in 16 sample loops of 0.5 mL in volume each and kept at low enough pressure and high enough temperature to not condense the higher molecular weight species and also to seize the reaction. With this setup 16 samples can be collected in a short period of time either to study the effect of residence time on gas phase compositions by moving the probe or the effect of reaction time on CNT growth by holding the probe constant. The GC was specially designed and modified in order to analyze smaller species like H_2 and CO and higher molecules like biphenyls in one injection. Figure 2 illustrates our preliminary results on species mole fractions in the gas phase during CNT growth.





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