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Kinetic study of multi walled carbon nanotubes synthesis by thermocatalytic decomposition of methane using floating catalyst chemical vapour deposition

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Highlights

- Synthesis of multiwalled carbon nanotubes(MWCNTs) using floating catalyst CVD.
- Investigation of mechanism of formation of MWCNTs.
- Investigation of rate controlling step and kinetics of formation of MWCNTs.

1. Introduction

Carbon nanotubes (CNTs) is one of the most widely explored research areas in materials science in the last two decades[1]. Extraordinary properties and wide range of applications of CNTs have fuelled the interest of researchers and scientist across the globe in the large scale synthesis of this nanomaterial. Chemical vapour deposition (CVD) method is one of the easiest method to scale-up production capacity of CNTs at a viable cost[2]. Substantial efforts have been made by scientific community in order to understand the growth mechanism and effects of operating parameters on the type and quality of CNTs produced. In order to have robust design methodology for the synthesis of CNTs, reaction mechanism, rate controlling step and overall rate of reaction involved in the synthesis must be known. Most of the prior studies have concluded bulk diffusion of carbon into the corresponding catalyst (metal) as the rate - limiting step, since the calculated activation energy(Ea) is in good agreement with values reported by Baker and co - workers[3] for Ea required for bulk diffusion of carbon. However, it must be noted that Bakers and coworkers had reported comparison of calculated Ea with energy required for bulk diffusion of carbon through metals in the solid state and not in the liquid state. Since, the catalyst particles are in liquid state at the reaction conditions, determination of rate limiting step by comparison of Ea seems to be invalid . In this paper, the kinetic studies were carried out for the synthesis of MWCNTs by thermocatalytic decomposition of methane using ferrocene as catalyst by floating catalyst CVD(FC-CVD) technique. Different kinetic models were compared and model with good agreement with experimental data was chosen in order to decipher rate controlling step.

2. Methods

MWCNTs were synthesized by the FC-CVD method in a two zone horizontal tubular quartz reactor. Methane, ferrocene and argon were used as carbon source, catalyst and inert gas respectively. Fixed amount of ferrocene were taken in a quartz boat and placed inside the reactor. As the evaporated ferrocene molecules crack in the gas phase and/or on the surface of the quartz tube , iron atoms or clusters deposit on the wall. Methane molecules undergo decomposition by adsorbing on the iron nanoparticles leading to the growth of CNTs. Effects of various parameters such as temperature(1073 K to 1273 K), catalyst concentration(0.2 to 4.6 mol m^{-3}) and partial pressure of methane(7 to 25 kPa) on the rate of decomposition of methane were studied.

3. Results and discussion

Characterization of MWCNTs: TEM images shown in figure of MWCNTs synthesized at 1273 K depicts clusters of tubes with uniform diameter distribution. Raman spectroscopy was carried out in order to confirm the presence of MWCNTs with high crystallinity. The BET surface area of purified MWCNTs sample was found to be 150 m^2/g . Thermogravimetric studies were performed to investigate the purity of the samples. It was found that with increase in synthesis temperature amount of impurities(amorphous carbon, iron etc) decreased.

Reaction kinetics: Activation energy for the formation of MWCNTs was calculated using Arrhenius equation which was found to be 1.45 eV. Effect of partial pressure on the rate of decomposition of methane at different temperature was studied and various kinetic models were used in order to determine the rate limiting step. Irreversible dissociation of adsorbed methane followed by irreversible decomposition of the adsorbed methyl group was found to be rate determining step.

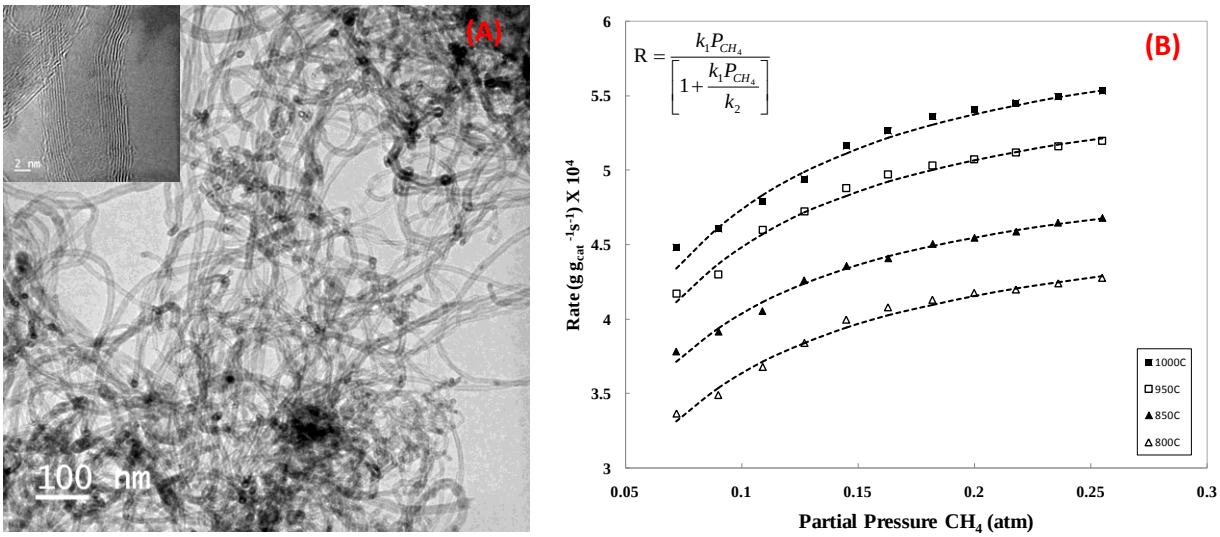

Figure 1. (A) TEM image of MWCNTs synthesized at 1000 ^{0}C. Inset HR-TEM image. (B) Effect of partial pressure of methane of rate of formation of MWCNTs at different temperature. Points are the experimental values and ----- lines are from simulation

4. Conclusions

1. MWCNTs were synthesized using FC-CVD. Methane and argon have been used as the source of carbon and carrier gas, respectively. Ferrocene has been used as the catalyst.
2. The formation mechanism of CNTs by FC-CVD technique comprises of seven steps namely. (1) Transport of the carbon source (hydrocarbon gas) from bulk to the surface of the catalyst. (2) Adsorption of reactant(hydrocarbon) on the the catalytic surface (active sites). (3) Surface reaction of adsorbed molecule to produce carbon atoms/molecules, (4) Dissolution of carbon molecules in the catalyst, (5). Saturation and supersaturation of carbon molecules in the catalyst. (6) Nucleation and growth of CNTs. (7). Transport of the gaseous products and hydrogen from the catalytic surface to the bulk.
3. To determine the rate determining step, multiple experiments were performed over a wide range of catalyst concentration(0.2 - 4.6 mol m^{-3}), temperature(1073K - 1273K) and partial pressure of methane(7 to 25 kPa). It was found that the irreversible dissociative adsorption of methane on the catalytic active site followed by the irreversible decomposition of the adsorbed methyl group is the rate controlling step with Ea of 1.45 eV.
4. MWCNTs synthesized were found to be with uniform diameter distribution with outer diameter in the range of 9.5 to 12.6 nm.

References

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Keywords
Floating catalyst; Ferrocene; Raman spectroscopy; Kinetics.