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Growth of multi-walled C nanotubes from pre-heated CH_4 using Fe_3O_4 as a catalyst precursor

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ABSTRACT

The present study aims to investigate influence of pre-heating of CH_4 on the growth of multi-walled C nanotubes (MWCNTs) on a Si (100) substrate by chemical vapor deposition technique using Fe_3O_4 powder as catalyst precursor. Reduction behavior of Fe_3O_4 was also studied in a flowing undiluted CH_4 atmosphere in order to gain better insight into MWCNT synthesis. Mass measurements, XRD and thermodynamic analyses were carried out to determine the extent of reduction of Fe_3O_4 by CH_4. It was found that Fe_3O_4 initially transformed to Fe via FeO within 30 min at 1200 K. Fe_3C and C then formed as reaction time increased to 60 min. It was postulated that reduction of Fe_3O_4 took place by H_2, a product of CH_4 decomposition. The overall reactions leading to the formations of Fe and Fe_3C phases were proposed using equilibrium thermodynamic analysis and the experimental results. Undiluted CH_4 was used to synthesize MWCNTs at temperatures in the range of 1050–1300 K. It was observed that a dense carbon coating was formed at 1300 K owing to self pyrolysis of CH_4, while at 1200 K individual MWCNTs were observed on the Si substrate. Growth of MWCNTs did not take place at the temperature range of 1050–1150 K. The use of CH_4 pre-heated at 1200 K, however, yielded MWCNTs at this temperature range. Experimental results and thermodynamic analysis of the C–H system (excluding graphite) indicated that pre-heating treatment of CH_4 promoted Fe_3O_4 reduction by H_2 and C formations from active intermediate hydrocarbon species of high molecular weights (especially C_6H_6).

1. Introduction

MWCNTs are novel materials with unique properties (e.g. high stiffness, strong axial strength, large surface area) for potential applications such as chemical sensors, catalyst supports and high performance composites [1]. They are commonly synthesized by chemical vapor deposition (CVD), laser ablation and arc discharge techniques [2]. Among these techniques, CVD offers inherent advantages such as better control of process parameters, high scalability to large areas and low cost. Numerous transition metal catalysts are used for the synthesis of MWCNTs by CVD technique [3–6]. The catalysts are generally prepared by (i) pre-reduction of metal compounds (e.g. salts, nitrates, oxides,) typically dispersed on a ceramic support by H_2, (ii) pyrolysis of metallorganics (e.g. ferrocene) and (iii) deposition of thin films of the metals or their oxides on a substrate followed by annealing or etching or reduction, prior to feeding C-containing gases into the growth chamber [7,8]. Various C sources including CO, and CH_4 usually diluted with H_2, He or Ar are used to produce C nanotubes by CVD technique. The MWCNT growth essentially involves decomposition of C-containing gas, diffusion and precipitation of C on the catalyst particle surfaces [9,10].

In our earlier work [11], we reported that pre-heating treatment of CH_4 at 1200 K prompted synthesis of MWCNTs at the temperature range of 1050–1150 K by Fe–Ni (70 wt.%) catalyzed chemical vapor deposition technique. We extended the previous work to the Fe_3O_4–CH_4 system because catalyst composition is known to affect MWCNT growth. The Fe–Ni (70 wt.%) alloy catalyst used in the previous study was already in metallic state, while in the present work it was initially Fe_3O_4. The main questions that stimulated us to carry out the present study were as follows: (i) could Fe_3O_4 reduction and MWCNT growth take place in a flowing, undiluted CH_4 atmosphere? (ii) what is the effect of preheating of CH_4 on these processes? and (iii) what is the thermochemistry behind them? The present study reports findings on these issues by means of XRD, mass measurements, SEM–EDX and thermodynamics. Furthermore, the thermodynamic calculation reported in the earlier work was limited to a single reaction of CH_4 decomposition. Whereas, in the present study, equilibrium thermodynamic analyses of the Fe–O–C–H and C–H systems were carried out in order to get a deeper insight into the Fe_3O_4 reduction and MWCNT growth processes. It should be noted that undiluted CH_4 was used as both reducing agent and C source because it is relatively cheap, abundant (the principal component of natural gas) and environmentally friendly.

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2. Equilibrium thermodynamic analysis in the Fe_3O_4–CH_4 system

Equilibrium thermodynamic analysis was performed by the method of minimization of the Gibbs' free energy of a system [12,13] at atmospheric pressure as a function of the temperature (1000–1300 K) and input reactant composition (X_C). X_C was defined as $n^o_C/(n^o_{Fe}+n^o_C)$ where n^o_C and n^o_{Fe} represent the initial number of moles for C and Fe. Input ratios of Fe to O and C to H were kept constant at 3:4 and 1:4 to simulate Fe_3O_4 and CH_4, respectively. In the system of interest, 25 species were considered to be as the constituents of the gas phase including CH_4, H_2, CO_2, CO, H_2O, H_2CO, CH_3, $Fe(OH)_2$, C_6H_6 and C_2H_4. Solid equilibrium phases were assumed to be C, Fe, Fe_3C, FeO, Fe_2O_3 and Fe_3O_4. Input thermodynamic data in the form of Gibbs' free energy of the formation of the constituents were obtained from the published thermochemical tables [14].

Fig. 1 depicts equilibrium stability diagram for the condensed phases constructed from the calculated results. As seen from the diagram, at temperatures between ~1005 and 1300 K, Fe_3O_4+FeO phase field is present up to ~0.1 C mol fraction (X_C) above which FeO, FeO + Fe, Fe, Fe + Fe_3C, Fe_3C and Fe_3C + C phase fields appear successively as X_C increases. At 1000 K, FeO + Fe_3C and FeO + Fe_3C + Fe phase fields are also seen for X_C values ranging from ~0.2 to 0.5. The major components of the gas phase are predicted to be H_2O, CO_2, H_2, and CO. Based on the thermodynamic results presented here, the overall dominant reactions leading to the formations of the major gaseous and solid species may be expressed by

$$2Fe_3O_{4(s)} + {}^{1}\!/_{2}CH_4 \rightarrow 6FeO_{(s)} + H_2O + {}^{1}\!/_{2}CO_2 \qquad (1)$$

$$Fe_3O_{4(s)} + 4CH_4 \rightarrow 3Fe_{(s)} + 4CO + 8H_2 \qquad (2)$$

$$Fe_3O_{4(s)} + 5CH_4 \rightarrow Fe_3C_{(s)} + 4CO + 10H_2. \qquad (3)$$

3. Experimental procedures

Fe_3O_4 powder with particle sizes <50 nm was used as catalyst precursor for the growth of MWCNTs by chemical vapor deposition technique. Prior to CVD experiments, Fe_3O_4 powder was blended in ethanol by ultrasonic agitation. The substrates cut from a silicon wafer with a <100> orientation were then dipped into the ethanol bath containing Fe_3O_4 particles. After ethanol was evaporated, the substrate with Fe_3O_4 catalyst precursor particles was then inserted into the CVD reactor.

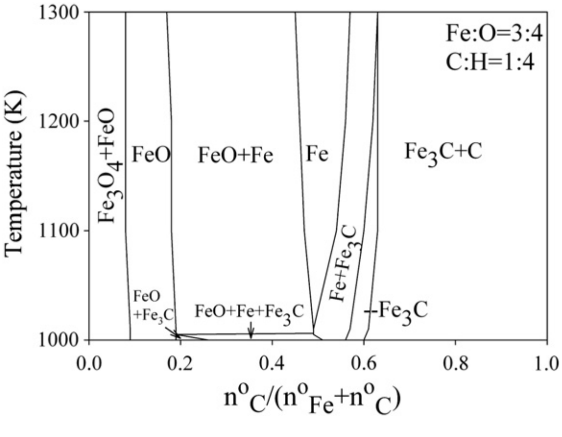

Fig. 1. Solid stability diagram in equilibrium with gas phase as a function of temperature and input C mole fraction (X_C) in the Fe–O–C–H system. X_C is defined as $n^o_C/(n^o_{Fe}+n^o_C)$, where n^o_C and n^o_{Fe} represent the initial number of moles of C and Fe. The input C:H and Fe:O ratios were kept constant at 1:4 and 3:4 for the calculations, respectively.

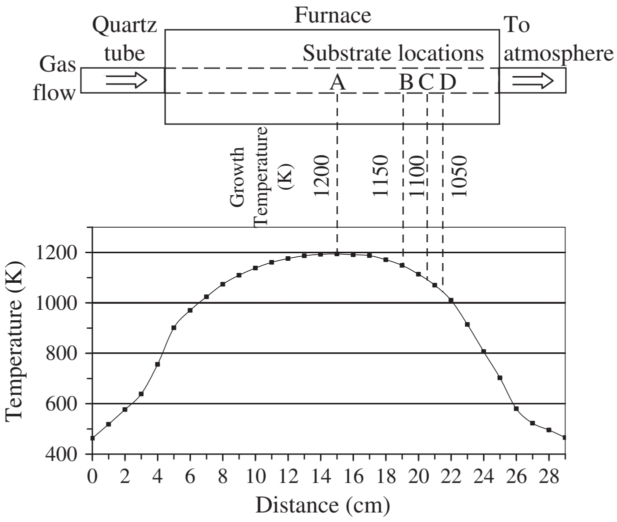

Fig. 2. A schematic presentation of the substrate positions in the furnace used and a temperature profile for the hot zone temperature (location A) set at 1200 K. Locations B, C and D in the low temperature zone donate the reaction temperatures at 1150, 1100 and 1050 K, respectively, while the hot zone temperature is at 1200 K.

MWCNT synthesis experiments were carried out in a horizontal tubular CVD reactor equipped with SiC heating elements, a quartz tube (20 mm in diameter, 500 mm in length) and gas flow meters. Two routes were used to reveal the effect of pre-heating of CH_4 on the MWCNT growth. In the first route, CH_4 without pre-heating was allowed to flow over the substrate placed in the hot zone of the furnace set at 1050, 1100, 1150, 1200 and 1300 K. Hot zone temperatures were measured independently by an external thermocouple (S type) at the central part of the reaction chamber designated as location A in Fig. 2. The temperature profile of the furnace with the hot zone temperature at 1200 K is also given in the figure. The profiles for the other hot zone temperatures are not shown here for the sake of clarity, but can be found elsewhere [15]. In the second route, the substrates were positioned at the low temperature zone by downstream side of the furnace at locations donated as B, C and D in Fig. 2 corresponding to the reaction temperatures of 1150, 1100 and 1050 K, respectively, while the hot zone temperature was kept at 1200 K. Thus, it was possible to intentionally pre-heat CH_4 as it passed through the hot zone prior to reaching the substrate. The flow rate of CH_4 was held

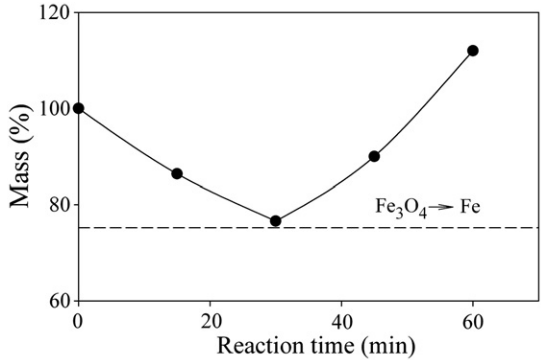

Fig. 3. Variation of the sample mass with reaction time in a flowing CH_4 atmosphere at 1200 K. The starting sample is Fe_3O_4 powder. Horizontal dashed line corresponds to the theoretical value (75.24 wt.%) for the transformation of Fe_3O_4 to Fe.