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A model for catalytic synthesis of carbon nanotubes in a fluidized-bed reactor: Effect of reaction heat

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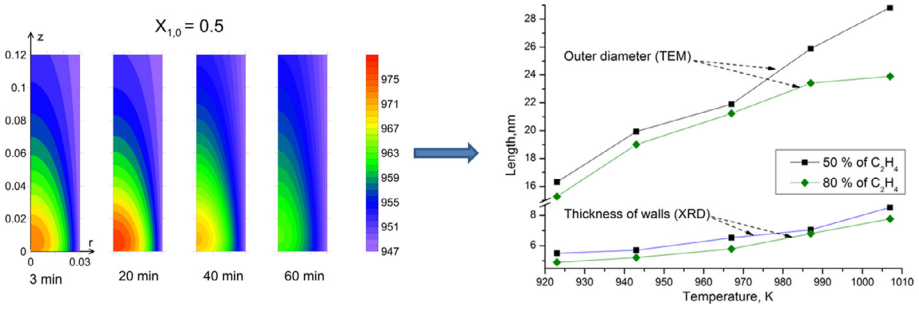
HIGHLIGHTS

- The improved quasi-continuous model of nanotube synthesis in fluidized bed reactor proposed.
- The overheating have shown to play a significant role for FB reactor with d > 6 cm.
- The reactor overheating affects the diameter, surface defectiveness, and amount of impurities.

GRAPHICAL ABSTRACT



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ABSTRACT

In the present study, we have developed a mathematic model describing quasi-continuous catalytic synthesis of multi-walled carbon nanotubes (MWCNTs) in a fluidized bed (FB) reactor. The special attention has been paid to the effects related to heat release or absorption during MWCNT synthesis. The heat of the reaction for MWCNT growth has been shown to significantly affect the thermal field in the reactor with the diameter as low as 6 cm. We attribute this to the extremely low thermal conductivity of aerogel-like MWCNT agglomerates (0.5–0.7 W/(m·K)), the basic units of the fluidized bed. According to the proposed model, the overheating up to 60 degrees takes place in the reactor with the diameter of D = 18 cm, the wall temperature of 943 K, and blown by 1:1 C_2H_4/Ar mixture. We have observed major changes caused by overheating: the activity of the catalyst and morphological properties of the produced MWCNTs (outer diameter, the structure of the walls, and fraction of impurities). The role of these thermal effects rises dramatically with increasing the reactor size and should be taken into account when designing reactors for large-scale production of MWCNTs.

1. Introduction

Multi-walled carbon nanotubes (MWCNTs) are unique class of the promising materials in fast developing nanotechnology due to their remarkable mechanical, chemical, and electronic properties. They have been already applied in a variety of devices and materials [1-3]. Different approaches and methods for MWCNT synthesis have been developed for the last 25 years [4]. Each of these methods requires specific facilities and conditions determining the type and the quality of the carbon nanomaterial as well as the performance and cost-efficiency of the process. Considering the industrial production of MWCNTs, the catalytic chemical vapor

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Nomenclature

Symbols

D	FB reactor diameter (m)
G	specific mass flux of gas mixture (per unit area of the horizontal section of the reactor) (kg/(m^2·s))
H	height of MWCNT fluidized bed (m)
I_{max}	maximum catalyst productivity (g of MWCNTs per 1 g of catalyst)
K_a	effective rate constant for catalyst activation (s^{-1})
K_T	effective rate constant for MWCNT growth (s^{-1})
k_0	effective rate constant for LCD growth (mole/(m^2·s))
m	mass (kg)
N_{rld}	total number of reloads;
R	FB reactor radius (m)
S	cross-sectional area of the reactor (m^2)
S_m	specific area of MWCNT (m^2/kg)
T	temperature (K)
X	relative molar concentration
u	gas flow velocity (at normal conditions, m/s)
W	reaction rate (kg/(m^3·s))
W_h	heat production rate (J/(m^3·s))
Y	relative mass concentration
z	vertical coordinate in fluidized bed (m)
ΔH	enthalpy of crystalline carbon formation from the gaseous carbon source (J/mole)
α	exponent in catalyst deactivation rate
γ_1, γ_2	mass stoichiometric factors for carbon source and hydrogen, correspondingly (per unit mass on carbon)
η	degree of catalyst deactivation
ρ	density (kg/m^3)
ξ	degree of catalyst activation
χ	lateral deposits mass fraction

Subscripts and superscripts

0	initial conditions
1, 2, 3	carbon source, hydrogen, inert gas
C	carbon
c	catalyst
g	gas
k	number of a reload
lt	lateral carbon deposits
nt	nanotubes
s	solid
S	reactor cross-section averaged
V	volume averaged
w	wall

deposition (CCVD) in a fluidized bed (FB) reactor is known to be the most suitable in terms of the productivity, product quality, and cost-efficiency [4]. Efforts to improve this technique [5-12] have facilitated the industrial production of MWCNTs reducing the price of the raw product almost by 100 times [13].

However, production of MWCNTs with tailored characteristics requires a full understanding of the relationship between MWCNT properties and the catalyst nature, growth conditions, apparatus design, and the process organization [9,11-13]. Despite a considerable amount of research on the kinetics of MWCNT synthesis performed, the general kinetic model is still challenging [11]. A detailed analysis of the kinetics data on the MWNCT synthesis via CCVD has been performed in [12,14,15]. Authors of the [15,16] have studied kinetics of MWCNT growth from ethylene on a Co-based catalyst in a plug-flow rector, as well as mass transfer and catalyst deactivation rate in moderate temperature range (758–923 K and 873–973 K, respectively). Despite the different expressions for the rates of MWCNT formation and catalysts deactivation, the kinetic data obtained in various works was similar: the first-order kinetics of MWCNT formation with respect to ethylene concentration and second-order catalyst deactivation with respect to the ethylene conversion in MWCNT agglomerates. It should be mentioned, that the first order dependence of MWCNT growth rate with respect to carbon-containing gas precursor was observed also in [12,17].

The MWCNT agglomerate growth was studied by optical monitoring in [18] for Co-based catalysts and ethylene as a precursor. It was shown that there is a significant increase in the size of agglomerates as a result of the synthesis of MWCNTs. The analysis of the resulting agglomerates have confirmed an earlier proposed mechanism of sub-agglomerates formation and subsequent sticking due to MWCNT entanglement [19]. As to presently existing mathematical models of the catalytic synthesis of CNTs, as a process in general, they are limited to the consideration of an ideal plug-flow reactor or 1D flow reactor with diffusion, as, for example, in [16].

The industrial application of the CCVD synthesis of MWCNTs in reactors with fluidized beds deals with certain engineering challenges. For example, high activity of catalysts and low bulk density of MWCNTs lead to dramatic increase of the bed volume during synthesis. We have recently developed quasi-continuous (cyclic) mathematical model describing experimental MWCNT synthesis in FB reactor [20]. The special attention has been paid to optimization of the cycle period, the parameters of loading and unloading of the reactor. The mathematical model of quasi-continuous process in FB reactor considers the following operation steps. Initial MWCNT powder placed in the reactor forms starting fluidized bed with minimal height at the temperature of reaction. Then, the reaction mixture (carbon source diluted with inert gas) as well as catalyst is supplied to the bed providing MWCNT growth. Unloading MWCNTs from the reactor (decreasing the fluidized bed height up to the initial value) ends the cycle and followed by consecutive loading an additional portion of the fresh catalyst. Such periodical procedure provides the production of nanotubes with desired purity (i.e. with minimal content of catalyst) and high conversion of gaseous carbon source. The model is based on experimental kinetic data and considers such processes as induction period of the catalyst activation and its further deactivation during the synthesis, as well as convective mass transfer of gaseous components. The model allows optimizing the operating mode for MWCNT synthesis to obtain maximum productivity and maximum average conversion of carbon-gaseous source [20].

In this study, the model of the CCVD synthesis of MWCNTs in fluidized bed reactor has been extended in order to take into account two new effects: (i) variation of temperature profile of the reactor due to the heat release or absorption during process, (ii) the formation of lateral carbon deposits (LCDs) via carbon source pyrolysis on the nanotube surface. Both factors influence the basic morphological, physical, and chemical properties of the nanotubes. The temperature variations during the synthesis cycle significantly affects both mean wall number (the average number of walls or, in other words, the average total thickness of the walls) and diameter of nanotubes, as well as growth rate of LCDs. Relation between lateral deposits and defectiveness of MWCNTs was recently studied in [21] on the basis of the analysis of Raman spectra. The present work considers the experimental kinetics of LCD