Considerations on the key precursor for the growth of carbon nanotubes using a diesel engine as a reactor

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HIGHLIGHTS

- A plausible precursor for carbon nanotube growth in a diesel engine was identified.
- The growth route of carbon nanotube in a diesel engine was considered.
- Modeling of carbon nanotube synthesis was performed.

GRAPHICAL ABSTRACT
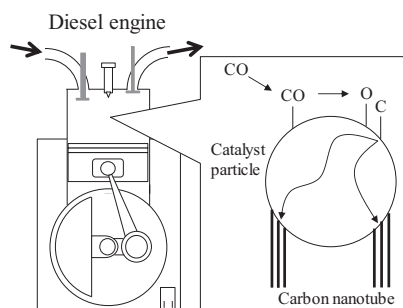
ABSTRACT

Carbon nanotube (CNT) was synthesized during combustion in a diesel engine by adding catalyst sources into fuel. Fuel used in this study was a mixture of normal dodecane/ethanol, methyl laurate/ethanol, and 1-decanol/ethanol. The analysis of an exhaust gas using a gas chromatograph revealed that the amount of carbon monoxide was most influential on the CNT formation than other factors such as adiabatic combustion temperatures and/or the amount of low molecular weight hydrocarbons like acetylene and ethylene. The significance of carbon monoxide in our system was also suggested by simulated and modeling works. Simulations of combustion reactions inside a cylinder were performed through CHEMKIN-PRO software for a qualitative evaluation. Modeling works of CNT growth rates were carried out by means of not only CO related reactions but also ethylene and acetylene related reactions as a source of carbon deposition. It was suggested that carbon monoxide had stronger connection with CNT synthesis in a diesel engine compared with other potential CNT precursors such as ethylene and acetylene. Furthermore, we proposed CNT growth route in our system by considering characteristics of combustion in a diesel engine.

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1. Introduction

Since carbon nanotube (CNT) possesses a lot of attractive physical properties, applications using CNT have been intensely expected. Accordingly, great efforts by many researchers have been devoted in order to effectively produce CNTs with high quality. Four CNT production processes have been proposed until now, such as arc discharge (Journet et al., 1997; Wang et al., 2009; Yoshida et al., 2008), laser ablation (Thess et al., 1996; Iijima et al., 1996), chemical vapor deposition (CVD) (Kobayashi et al., 2013; Tian et al., 2011; Chen et al., 2014; Castro et al., 2013; Quinton et al., 2015; Mas et al., 2016), and flame process (Diener et al., 2000; Vander Wal and Hall, 2001; Wen et al., 2008; Unrau et al., 2010; Masunaga et al., 2013; Hall et al., 2011; Oulanti

Nomenclature

ΔE_i activation energy of reaction rate constant k_i

ΔH_i: reaction enthalpy of reaction step (i)

K_A (=$K_1^2 K_2 K_3$)   integrated equilibrium constant in CO disproportionation reaction

K_B (=$1/K_1 K_3$)   integrated equilibrium constant in CO disproportionation reaction

K_C (=$K_8 K_9 K_{10}^2$)   integrated equilibrium constant in ethylene decomposition reaction

K_D (=$K_{12} K_{13} K_{14}$)   integrated equilibrium constant in acetylene decomposition reaction

k_i (=$k_{i0}\exp(-\Delta E_i/RT)$)   reaction rate constant of forward reaction of reaction step (i)

K_i (=$K_{i0}\exp[-\Delta H_i(1/T - 1/T_0)]$)   equilibrium constant of reaction step (i)

P_{C2H2} partial pressure of acetylene
P_{C2H4} partial pressure of ethylene
P_{CO} partial pressure of carbon monoxide
P_{CO2} partial pressure of carbon dioxide
P_{H2} partial pressure of hydrogen
R gas constant
R_{CNT} modeled CNT growth rate
T temperature

Superscript

$'$ ethylene related reaction/coefficient
$''$ acetylene related reaction/coefficient

et al., 2015; Hu and Lin, 2016). Among these processes, CVD methods have been most intensively studied and actually achieved the mass production of multi-walled carbon nanotube (MWNT) (Zhang et al., 2011). However, its production cost, especially single-walled carbon nanotube (SWNT), is still high, hence the reduction of production cost is still required. Recently, flame processes for synthesizing CNT have been focused on and recognized as a potential candidate for CNT production. As general characteristics, flame processes possess several advantages like easy scale-up, low investment costs. Thus, flame process is one of expected options to produce CNTs cost-effectively although CVD is also a promising candidate. In practice, there is a company, Nano-C, Inc., to produce CNTs commercially using the combustion process (Richter et al., 2008). Moreover, carbon black and fullerene which are known as an allotrope of CNT have been already produced commercially using the burner flame process and the production cost of such carbon materials have been significantly suppressed in comparison with conventional processes like arc discharge (Takehara et al., 2005; Arikawa, 2006). We believe this information stated above provides a motivation to study flame process further. The large difference between flame method for carbon black/fullerene production and that for CNT production is whether catalysts for growing such a carbon material are included in feedstock or not. Flame process for carbon black and fullerene does not require catalysts while that for CNT does. Although the reduction of CNT production cost using flame processes has been expected, a great challenge is anticipated; the availability of carbon and catalyst sources still remains low.

Our group has regarded a diesel engine as a combustion reactor to form nanomaterials and could successfully synthesize CNT as reported in preceding articles (Suzuki and Mori, 2017a, 2017b, 2018). It can be considered that a diesel engine is a potential candidate to produce CNT with low cost because a simultaneous power generation during CNT production is carried out. Moreover, a fuel injection system of a diesel engine has been modified recently from a mechanical control to an electrical control termed common-rail system. These improvements provided a diesel engine with an enhanced flexibility, resulting in a remediation of emission properties. This fact implies that a diesel engine is a promising candidate for the synthesis of nanomaterials due to a potential attainment of a suitable injection system for that purpose. In previous works employing a conventional mechanical type diesel engine, MWNTs were mainly synthesized using diesel fuel/ethanol mixing fuel (Suzuki and Mori, 2017) or mixing fuel of n-dodecane/ethanol, methyl laurate/ethanol and 1-decanol/ethanol (Suzuki and Mori, 2017, 2018) as carbon and heat sources, fer-

rocene as an iron catalyst source, and sulfur/molybdenum as a catalyst promoter. Since methyl laurate and 1-decanol are emerging biofuel in recent years, we employed them in our work. It was revealed in a previous report that MWNTs could be synthesized when both of a sulfur addition and an introduction of ethanol in fuel were satisfied (Suzuki and Mori, 2017). Most of synthesized CNTs were MWNTs with multiple layers although very little SWNT was grown (Suzuki and Mori, 2018). CNT yield was approximately 3 ppm at most on the basis of injected carbon weight (Suzuki and Mori, 2017, 2018). Tendencies stated above were independent on fuel type. Detailed information on geometric characteristics of CNTs such as length and diameter can be referred to our previous papers (Suzuki and Mori, 2017a, 2017b, 2018). The effectiveness of sulfur for CNT growth has been reported by some researches using CVD processes (Zhang et al., 2014; Wei et al., 2007; Alemán et al., 2016) where property changes due to sulfur addition such as the reduction of catalyst melting temperature, the decrease of catalyst surface energy etc. promoted CNT growth. It is reasonable to consider that similar effects behaved in our study. Although our previous works, to some degree, mentioned the factor which strongly affected CNT growth in a diesel engine (Suzuki and Mori, 2017, 2018), it was insufficient to explain the key CNT precursor and/or the CNT growth mechanism. Therefore, our major purpose in this work is to identify the key factor which contributes to CNT formation in our system, and to provide clues leading to understanding the CNT growth mechanism and/or CNT synthesis path in a diesel engine, taking into account experimental and modeling/simulated results.

2. Methods

2.1. Experiments

The diesel engine used in this study was a direct injection, 4-stroke cycle engine (KIPOR KDE.2.0E). N-dodecane (Wako Pure Chemical Industries, Ltd., 99.0+%), methyl laurate (Wako Pure Chemical Industries, Ltd., 98.0+%) and 1-decanol (Tokyo Chemical Industry Co., Ltd., >98.0%) were employed as main fuel. The latter two chemicals are biomass-derived materials and the significance using them was described in previous paper (Suzuki and Mori, 2018). Also, specifications of the diesel engine used in this study and chemical structures of main fuel were described elsewhere (Suzuki and Mori, 2018). Super dehydrated ethanol (Wako Pure Chemical Industries, Ltd., 99.5+%) was mixed with main fuel. The detailed procedures on how to prepare tailored mixing fuel were