論文 / 著書情報
Article / Book Information

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種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
Doctoral Program

論 文 要 旨

THESIS SUMMARY

専攻： Department of	化学工学　専攻	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of　（　工学　）
学生氏名： Student's Name	鈴木　俊介	指導教員（主）： Academic Supervisor(main)	森　伸介　准教授
		指導教員（副）： Academic Supervisor(sub)	

要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

A diesel engine has been utilized for a power source and/or electrical generator for more than one hundred years. On the other hand, the application of a diesel engine to other field has been considered in recent years. For instance, the utilization as a chemical reactor for the generation of syngas has been reported. In this study, a diesel engine was regarded as a combustion reactor to synthesize carbon nanomaterials such as carbon nanotube (CNT). CNT is quite promising nanomaterial because it possesses a number of outstanding physical/chemical properties. However, the applications using CNTs are limited even today due to its very high production cost. Flame process using a burner has been paid attention since not only CNTs but also the allotrope of CNT like carbon black and fullerene has been produced commercially in flame technique owing to its inherent characteristics such as easy scale-up and low investment cost. Similar features are provided for CNT formation process using a diesel engine. A diesel engine is an attractive system since simultaneous power generation and material synthesis can be achieved in one system, being expected that the CNT production cost is reduced in comparison with various conventional processes. Combustion reactions of injected fuel which provided adequate heat and carbon precursors were utilized for growing CNTs. Catalyst sources that were necessary for the synthesis of CNTs were also introduced into a reactor.

As a first step (Chapter 1), experimental conditions required for CNT formation in a diesel engine were examined when using a gas oil as base fuel. No CNT formation was observed when gas oil alone was employed even in the presence of catalyst sources. It was found that at least three conditions had to be satisfied for successful synthesis of CNTs, namely, (1) the introduction of catalyst precursor, (2) the usage of gas oil/ethanol mixing fuel, and (3) the addition of sulfur as an enhancer.

As a next step (Chapter 3), normal dodecane/ethanol mixing fuel was employed as base fuel in place of gas oil/ethanol because gas oil has very complicated compositions which makes some analyses difficult. Due to fixed compositions of fuel, the evaluation of the key factors such as combustion temperatures and gaseous species which contributed to CNT synthesis became possible. It was suggested that carbon monoxide affected CNT formation more strongly than a combustion temperature. Also, the analysis on catalytic nanoparticles revealed that sulfur seemed concentrated on iron catalyst.

Then, in Chapter 4, the impact of the molecular structure of fuel on CNT formation was investigated in the employment of fatty acid methyl ester (methyl laurate) and alcohol with long alkyl group (1-decanol) besides normal dodecane. This activity was motivated because combustion characteristics and emission properties were affected by the chemical structure of fuel according to a number of preceding papers. The

difference of results was observed when a volumetric percent of ethanol in initial fuel was low, while it became tiny along with an increase of an ethanol fraction. It was implied that this difference was probably interpreted by the amounts of carbon monoxide in an exhaust. Also, elemental analysis showed that the state of catalyst nanoparticles should not be oxidized one but the metallic one for the growth of CNTs.

In-depth discussion on a promising CNT precursor and CNT growth mechanism/pathway was carried out through experimental, computational and modeling approaches (Chapter 5). Experimental approach employed an exhaust gas analysis, and combustion reactions were simulated in computational approach. The modeling of CNT growth reactions using CO, C_2H_4 and C_2H_2 as a carbon source were exploited based on several elemental reactions. All of them indicated that carbon monoxide might behave as a central role in CNT formation rather than other hydrocarbons like acetylene and ethylene. Also, it was suggested that fuel rich region was of advantage in forming gaseous carbon precursor and appropriate growth of catalyst nanoparticles. Given the combustion characteristics of a diesel engine, CNT synthesis might take place in fuel rich regions like the vicinity of fuel injection nozzle and/or the center of sprayed fuel.

In order to improve CNT productivity, the impacts of additional gaseous fuel were investigated (Chapter 6). H_2, CH_4 and C_2H_2 were selected as additional intake gas. A slight increase of CNT growth was found in the use of H_2 and CH_4, while CNT production was degraded in C_2H_2. This might be attributed to very high concentration of acetylene which deactivated catalysts at early reaction stage when C_2H_2 was employed as additive gaseous species.

Finally, in Chapter 7, the role of sulfur as a promoter in CNT growth was examined by means of chemical vapor deposition (CVD) process because the addition of sulfur was one of key factors for the successful CNT synthesis in a diesel system. In order to make analysis easier, CVD technique was employed. The introduction of sulfur significantly reduced the activation energy required for CNT growth which was revealed by Arrhenius plot. The shift of the rate-determining step in carbon diffusion process during CNT growth might take place in the presence of sulfur. According to some analyses on catalytic nanoparticles, it was suggested that the reduction of melting temperature of catalysts might occur, resulting in the enhancement of CNT synthesis.

In Chapter 8, overall summary obtained in this study and future works are described.