PRODUCTION OF CARBON NANOFIBERS/TUBES FROM VARIOUS ALCOHOLS USING THE LIQUID PULSE INJECTION TECHNIQUE

Shin R. Mukai, Atsushi Ikeshita, Hitoshi Shibashita and Riku Furukawa

Division of Chemical Process Engineering, Graduate School of Engineering, Hokkaido University, Sapporo, Japan

Introduction

Carbon nanofibers/nanotubes (CNFs/CNTs) have many unique properties, and the usage of them in various fields is expected. However, due to the high production costs of CNFs/CNTs, applications in which the usage of them is thought to be feasible is still quite limited.

Previously, we introduced a new method to efficiently produce CNFs/CNTs, the liquid pulse injection (LPI) technique [1-2]. The main feature of this method is the introduction of the fiber source into the reactor as liquid pulses. Such liquid pulse introduction enables the generation of extremely active catalyst particles in a highly dense state [3]. Therefore, CNFs/CNTs can be easily obtained at high carbon yields through this method. We also experimentally showed that CNFs/CNTs can be obtained at high carbon yields even from an inexpensive sources, such as mixtures of benzene, toluene and xylene [4].

Aromatics are generally used as the carbon source for CNF/CNT production. However, such hydrocarbons are usually highly toxic, and many regulations exist for the usage of them. Therefore in this work, we examined the possibility of the efficient synthesis of CNFs/CNTs from a much safer, and in some cases renewable, source, alcohols.

Experimental

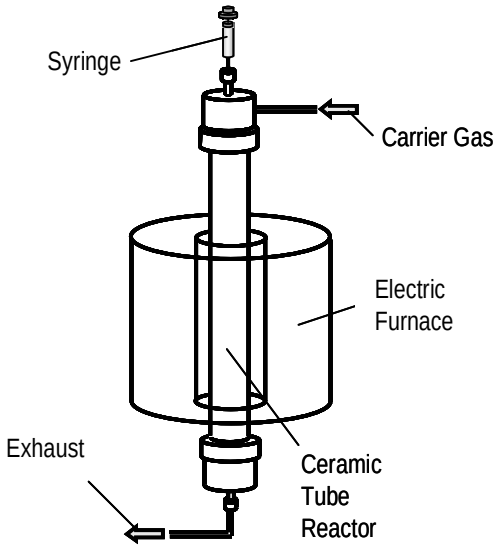

Fig. 1 Schematic of Experimental Apparatus

Figure 1 shows a schematic of the apparatus used in this work for CNF/CNT production. It is equipped with a tube reactor, 2 stainless steel joints and an electric furnace. A ceramic tube with an inner diameter of 85 mm and a length of 1200 mm, was used as the reactor. H_2 was used as the carrier gas, and a mixture of ferrocene, the carbon source and thiophene (catalyst promoter) was used as the starting material. 4 alcohols, methanol, ethanol, 2-propanol and 1-butanol, were used as the carbon source. First the reactor was thoroughly purged with N_2, and then H_2 was introduced to the reactor. Next the temperature of the reactor was raised to 1,200ºC using the electric furnace. After the temperature distribution in the reactor reached a steady state, liquid pulses of the starting material were intermittently introduced into it at an interval of 60 s. During CNF/CNT production, the composition of the reactor outlet gas was monitored using a micro GC. Then after 60 s from the injection of the final liquid pulse, the reactor was quickly purged with N_2, and the electric furnace was turned off. The reactor was cooled down to room temperature, and the produced CNFs/CNTs located at the bottom of the reactor were collected and weighed. The carbon yield was calculated as the ratio between the amount of carbon collected as CNFs, and the amount of carbon introduced into the reactor. The amount of pyrolytic carbon formed on the reactor wall was evaluated by oxidizing it using air, and measuring the amount of CO_2 formation. Finally, the carbon balance was calculated.

Results and Discussion

Figure 2 shows SEM images of typical CNFs/CNTs obtained in this work. CNFs/CNTs could hardly be obtained when methanol was used as the carbon source, but they could be obtained at noticeable carbon yields when other alcohols were used. Although the carbon yield values were lower than those achieved when aromatics were used as the carbon source, they were still higher than those attainable using other production methods. Interestingly, the carbon yield increased with the increase in the carbon to oxygen ratio (C/O) of the alcohol.

Next, we quantified all of the products obtained during CNF/CNT production, and calculated the carbon balance. The results are summarized in Fig. 3. It was found that a significant amount of CO was generated during CNF/CNT production. The amount of oxygen in this CO was almost equal to the amount of oxygen in the original carbon source, which indicates that the provided oxygen leaves the reactor in the form of CO, and this CO doesn't contribute to the growth of CNFs/CNTs. This means that the decrease in carbon yield cannot be avoided when alcohols are used as the carbon source, and that this decrease will be significant when the C/O ratio of the alcohol is low. As the C/O ratio of methanol is unity, no carbon will be available from this alcohol, but the carbon in the ferrocene and thiophene seemed to have contributed to the growth of a trace amount of CNFs/CNTs.

Finally, we verified the possibility of utilizing the CO generated from the alcohols. In order to produce CNFs/CNTs

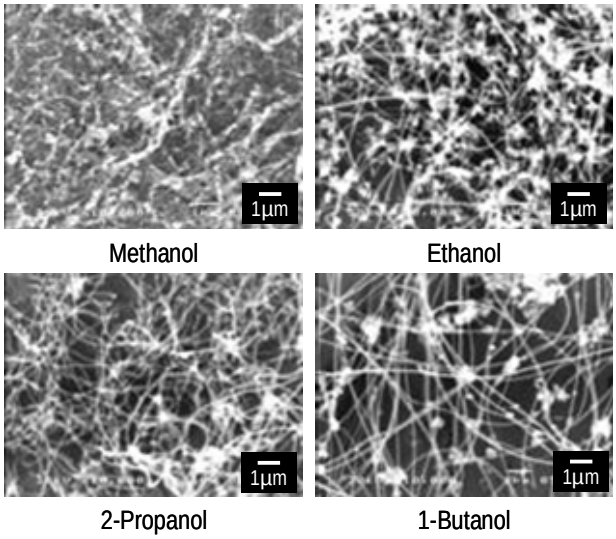

Fig. 2 SEM Images of Typical CNFs/CNTs Obtained in This Work

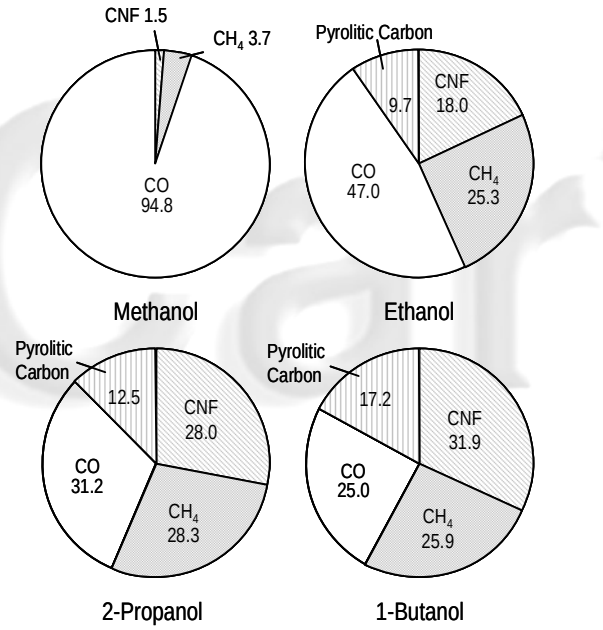

Fig. 3 Carbon Balance

using ultra-fine metal catalyst particles, the particles must be kept in a reduced atmosphere so that they can maintain their catalysis. Therefore reducing gases such as CO and H_2 are typically used as the carrier. As a significant amount of CO and also H_2 is generated when alcohols are used as the carbon source, it is assumed that a reduced atmosphere will be naturally formed in the field where CNFs/CNTs grow. This means that the function required of the carrier is only to sweep out the products from the reactor without disturbing their growth. Therefore, we attempted to produce CNFs/CNTs from alcohols using an inexpensive inert gas nitrogen as the carrier.

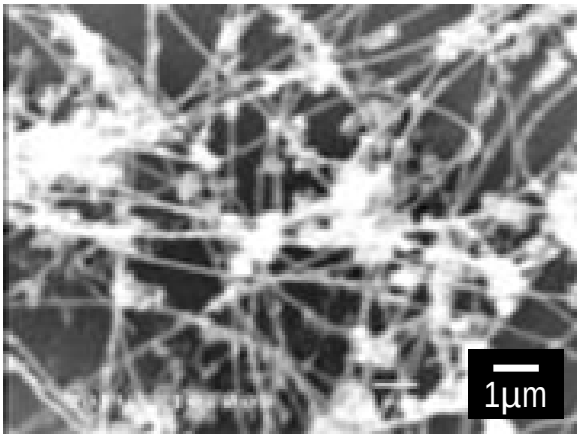

Fig. 4 SEM Image of CNFs/CNTs Obtained Using N_2 as the Carrier Gas

Although the purity decreased, it was found that a significant amount of CNFs/CNTs could be obtained (Fig. 4).

Conclusions

In this work, we attempted to efficiently synthesize carbon nanofibers/nanotubes (CNFs/CNTs) from various alcohols using the LPI technique, a method developed by the authors for the efficient production of filamentous carbons. We found that CNFs/CNTs can basically be obtained from any type of alcohol. Through exhaust gas analysis, it was found that the oxygen in the alcohols leaves the reactor in the form of CO, therefore the carbon yield will decrease with the decrease in the carbon to oxygen ratio of the alcohol. However, by utilizing the generated CO and H_2 which are also generated from the alcohols, we found that carbon CNFs/CNTs can be obtained even when an inexpensive gas, N_2, is used as the carrier.

Acknowledgments. This work was partly supported by the Japan Science and Technology Agency (JST) through the Research for Promoting Technological Seed program (2009).

References

[1] Mukai SR, Ohtaka T, Tamon H. Production of carbon nanofibers using the Liquid Pulse Injection technique. Extended abstracts, Carbon 2003 Oviedo (Spain), 2003
[2] Mukai SR, Ohtaka T, Tamon H. High efficiency carbon nanofiber production using the Liquid Pulse Injection technique. Extended abstracts, Carbon 2004 Providence (Rhode Island, USA), 2004
[3] Hisamatsu O, Mukai SR, Shirato Y, Tamon H. High efficiency carbon nanofiber production from mixtures of benzene, toluene and xylene using the liquid pulse injection technique. Extended abstracts, Carbon 2006 Aberdeen (United Kingdom), 2006
[4] Mukai SR, Masuda T, Matsuzawa Y, Hashimoto K. The Influence of Catalyst Particle Size Distribution on the Yield of Vapor-Grown Carbon Fibers Produced Using the Liquid Pulse Injection Technique. Chem. Eng. Sci. 1998;53:439-448.