HIGH EFFICIENCY CARBON NANOFIBER PRODUCTION USING THE LIQUID PULSE INJECTION TECHNIQUE

Shin R. Mukai, Takeshi Ohtaka, Hajime Tamon
Department of Chemical Engineering, Graduate School of Engineering, Kyoto University
Katsura, Kyoto 615-8510, Japan

Corresponding author e-mail address: mukai@cheme.kyoto-u.ac.jp

Introduction

Previously we introduced the Liquid Pulse Injection (LPI) technique, a new method which allows the production of vapor grown carbon fibers (VGCFs) at extremely high growth rates [1,2]. VGCFs as long as 50 mm can be obtained within 30 s by using this method. In this method, the catalyst source, typically a benzene solution of ferrocene, is injected into the reactor as a liquid pulse. This is thought to lead to the generation of numerous active catalyst particles which can produce VGCFs at extremely high growth rates. Recently, we experimentally showed that carbon nanofibers (CNFs) could also be efficiently produced by modifying this LPI technique [3]. This work was conducted to clarify the influences of experimental conditions on the growth behavior of CNFs produced by the LPI technique.

Experimental

The experimental apparatus originally used for VGCF production was employed in this work [1]. Hydrogen was used as the carrier gas. Benzene and ferrocene were respectively used as the carbon source and catalyst source. After the carrier gas flow reached a steady state and the temperatures of the gas preheating zone and reaction zone respectively reached 1073K and the desired temperature which was set between 1273 K and 1373 K, 20 liquid pulses of a mixture of the carbon source and catalyst source were injected into the reactor at an interval of 60 seconds. After 60 seconds passed since the final pulse was injected, the reactor was rapidly cooled to room temperature, and the materials caught in the inner tube placed in the reactor were collected. The obtained samples were weighed and directly observed by a scanning electron microscope (SEM, JEOL Ltd.; JSM-6340FS). Experiments in which the total

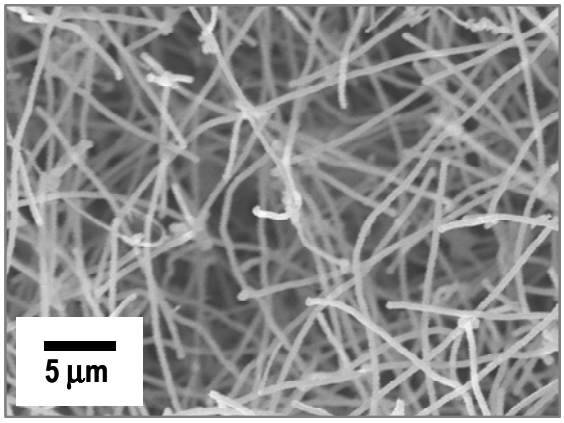

Fig. 1 SEM image of typical CNFs obtained in this work

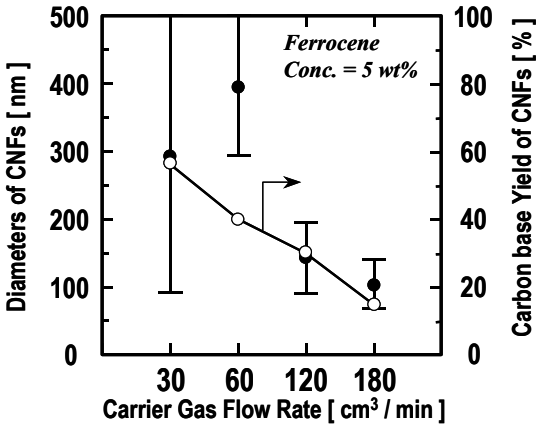

Fig. 2 Effects of carrier gas flow rate on CNF diameter and yield

reactor outlet gas was collected and subsequently analyzed by gas chromatography were also conducted. The influences of experimental conditions, such as the carrier gas flow rate, and reaction temperature were thoroughly investigated.

Results and Discussion

Figure 1 shows a SEM image of a typical sample obtained in this work. The image shows that the sample mostly includes CNFs and impurities such as carbon particles can hardly be found. Therefore, although the samples collected from the inner tube may include a small amount of impurities, they will be treated as pure CNFs hereafter. The diameters of the fibers were fairly uniform, and were in the range of 40 nm to 500 nm, depending on production conditions.

It is expected that among the investigated conditions, the carrier gas flow rate will have the largest influence on the diameters and yields of CNFs. When the carrier gas flow rate is increased, the residence time of the generated fibers becomes shorter, therefore the carbon yield and fiber diameter are expected to decrease. Figure 2 shows the dependencies of the carbon yield and fiber diameter on the carrier gas flow rate. The temperature of the reaction zone, concentration of ferrocene in the liquid pulse and volume of an individual pulse were respectively fixed to 1373 K, 5 wt% and 20 μl in this series. Note that the carbon yield was calculated as the ratio between the amount of carbon included in the CNFs and the carbon included in the material introduced into the reactor. It can be noticed that not only the expected trend holds, but also that CNFs can be obtained at carbon yields as high as 58 %.

Through material balance calculations it was confirmed that under the conditions investigated in this work, over 95% of the carbon introduced into the reactor was collected as CNFs and pyrolytic carbon deposited on the reactor wall. Gas products were hydrogen and a small amount of methane, therefore this process practically converts benzene to carbon and hydrogen.

Experiments were also conducted at 1273 K. Thin CNFs with diameters in the range of 40 to 60 nm were obtained, but the carbon yields that they were obtained at were only a few percent. These results show that the high productivity of CNFs achieved at 1373 K highly owes to the catalytic activities of the generated catalyst particles. As active catalyst particles can be easily generated in the LPI technique, this method is thought to be an ideal method for CNF production.

Conclusions

The influences of experimental conditions on the growth behavior of CNFs produced by the LPI technique were clarified. It was found that the productivity of CNFs highly depends on the activity of the generated catalyst particles. By adjusting experimental conditions, CNFs could be obtained at carbon yields as high as 58%.

References

[1] Masuda T, Mukai SR, Hashimoto K. The Liquid Pulse Injection Technique: a New Method to Obtain Long Vapor Grown Carbon Fibers at High Growth Rates. Carbon 1993;31(5);783-787

[2] 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(3);439-448

[3] Mukai SR, Ohtaka T, Tamon H. Production of carbon nanofibers using the liquid pulse injection technique. Extended abstracts, Carbon 2003 (Oviedo, Spain): Spanish Carbon Group, 2003.