THE PRODUCTION OF CARBON FIBERS FROM LIGHT PARAFFINS
IN THE GAS PHASE

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INTRODUCTION

Vapor grown carbon fibers (abbreviated to VGCFs) grow in the axial direction through the catalysis of ultra-fine metal particles (e.g. iron). They grow in the radial direction as pyrolitic carbon deposits on the surface of the fiber. Therefore, VGCFs are formed by carbon layers arranged like a tree-ring structure. VGCFs possess extremely high mechanical strength and electric conductivity, due to this unique structure. Since VGCFs can be obtained using one entrained bed, there is a possibility to drastically decrease the production cost of short carbon fibers.

Previously, we developed a new method to produce VGCFs, the liquid pulse injection (LPI) technique [1-4]. As highly active ultra-fine metal catalyst particles can be easily generated using this new technique, it is possible to rapidly grow VGCFs. Growth rates up to 3 mm$\cdot$s^{-1} are attainable when aromatics (e.g. benzene) are used as the carbon source [4]. VGCFs could also be obtained from light paraffins [5], which was considered not to be suitable for the production of VGCFs. This indicates the possibility of producing VGCFs from a wide variety of hydrocarbons using the LPI technique.

Considering the growth conditions of VGCFs, it is unlikely that they grow directly from the initial carbon source, when light paraffins are used. Secondary products generated from the decomposition of the initial material are thought to actually contribute to fiber growth. The aim of this work is to verify the hydrocarbon(s) which actually contributes to fiber growth when light paraffins are used as the initial carbon source for VGCF production.

EXPERIMENTAL

Experiments were conducted using the apparatus shown in Fig. 1 to analyze the components in the gas phase at the reaction zone of fiber growth. The reaction conditions were set as the same as those used when fibers were produced, but the catalyst source was not introduced into the reactor. The preheating zone and the reaction zone of the reactor used had the same shape as that used for fiber production, but the shape of the reaction zone was changed so that the gas could be rapidly quenched to terminate further gas phase reactions and be easily collected. The temperatures of the gases in the preheating and reaction zones were 1073 K and 1373 K, respectively. Three kinds of paraffins were used as the carbon source: i-butane, n-pentane, n-hexane. Benzene, a typical carbon source for fiber production, was also used. The initial concentration of each carbon source was in the

range 4.88 to 13.73 mol$\cdot$(m^3-NTP)$^{-1}$, and the reaction time was 30 min. The flow rate of the carrier gas (hydrogen) was 60 cm^3-NTP$\cdot$min^{-1}. After each experiment, the components of the sampled gas was identified using mass spectroscopy, and quantitatively analyzed using gas chromatography.

RESULTS AND DISCUSSION

Figure 2 shows the results of gas analysis. The main hydrocarbons obtained from each initial carbon source were benzene, methane and ethylene. From fiber production experiments, methane is thought not to contribute to fiber growth [4]. Ethylene may be a contributor, but the amount of it is extremely small in comparison with the mass of the produced VGCFs. Considering these facts, there is a high possibility that benzene is the actual main species that contributes to fiber growth. Therefore, we attempted to investigate the relationship between the concentration of benzene at the reaction zone, and the initial growth rate of the VGCFs produced from the same initial carbon source.

The initial growth rates of VGCFs were calculated from the growth curves obtained in our previous work [5]. The following empirical equations were employed:

$$dL/dt = A\exp(-Bt) \qquad (1)$$

$$L = A/B\{1-\exp(-Bt)\} \qquad (2)$$

where L is the fiber length, t the reaction time and A, B are adjustable parameters. These values were determined by adjusting the calculated curve of eq. (2) to the experimental results. Note that parameter A gives the initial growth rate of the fibers. Figure 3 shows the plot of the initial growth rates (A), against the initial carbon source concentration. The results of benzene are also shown for comparison. Though the values of light paraffins are smaller than those of benzene, the minimum value is over 1 mm$\cdot$s^{-1}, which is at least ten times larger than those of VGCFs produced by conventional production methods using benzene as the carbon source. In these methods, VGCFs are hardly obtained from light paraffins. Values over 2 mm$\cdot$s^{-1}, which is close to those of aromatics, were attained when n-pentane was used as the initial carbon source.

Figure 4 shows the relationship between the initial growth rate of the fibers, and the concentration of benzene at the reaction zone. All data lay well on one linear line, even though the initial carbon sources are different. This fact indicates that benzene is the
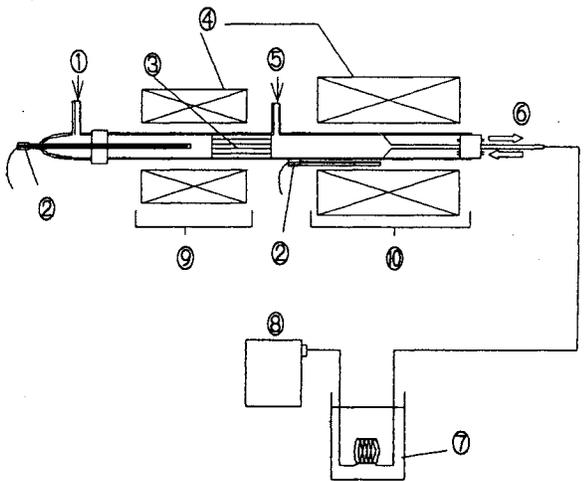
actual contributor to fiber growth.

CONCLUSION

From the analysis of the gas phase at the reaction zone of fiber production, it was found that although the initial carbon source is light paraffins, the main hydrocarbons which exist at the reaction zone are methane, benzene and ethylene. Among these hydrocarbons, the initial growth rate of the fibers has a linear relationship with the concentration of benzene, indicating the fact that benzene is the main hydrocarbon which contributes to fiber growth.

REFERENCES

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Fig. 2 Results of Gas Analysis

Fig. 3 Relationship between Initial Concentration and Initial Growth Rate

① CARRIER GAS INLET   ⑥ COOLING WATER
② THERMOCOUPLES   ⑦ LIQUID TRAP
③ HONEYCOMB   ⑧ GAS PACK
④ ELECTRIC FURNACES   ⑨ PREHEATING ZONE
⑤ CARBON SOURCE INLET ⑩ REACTION ZONE

Fig. 1 Experimental Apparatus

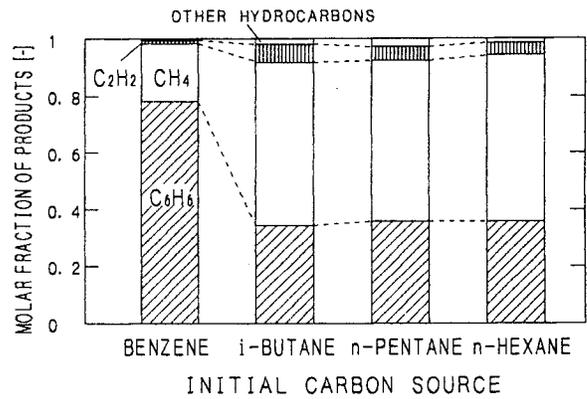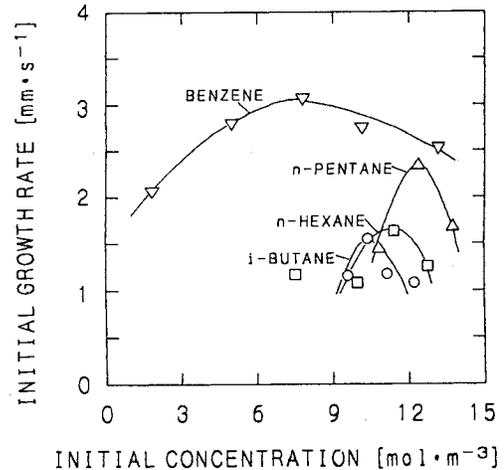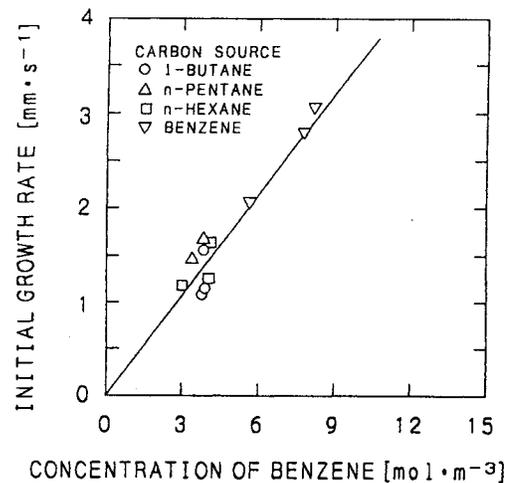Fig. 4 Relationship between Concentration of Benzene and Initial Growth Rate