GROWING CARBON FIBERS WITH AN IMPROVED GAS FORMULATION CONTAINING AMMONIA

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INTRODUCTION

It is well known that small particles of iron are able to grow macroscopic filaments of carbon in a pyrolyzing hydrocarbon atmosphere [1]. Furthermore, the addition of sulfur of approximately equimolar quantities to the Fe catalyst vastly increases the efficienty of fiber production [2,3]. This report describes how adding ammonia gas to the feedstock containing Fe particles and H_2S during fiber growth improves the length and uniformity of the fibers while reducing the amount of soot and other debris produced.

EXPERIMENTAL

This effect was investigated in two different growth reactors, one horizontal and one vertical (Figure 1). Each reactor utilized a mullite tube maintained at 1100°C. The feedstocks were a mixture of 99.99% pure methane, 99.99% pure ammonia, 99.3% pure H_2S, and He bubbled through 99.5% pure $Fe(CO)_5$ at 22°C .

As shown in Figure 1, the fibers were collected from the exhaust stream of each tube. The quality of fibers grown was assessed by dividing the mass of material produced by its uncompressed volume to obtain its apparent density. In general, longer fibers yielded lower apparent densities while soot yielded a density above 0.04 g/cm^3. Scanning electron microscopy provided an additional qualitative picture of average length and uniformity of fibers produced.

RESULTS

Figure 2 summarizes a series of experiments performed in the vertical system using 6 cm^3/min of H_2S, 155 cm^3/min of He bubbled through $Fe(CO)_5$, and 6,600 cm^3/min of various mixtures of methane and ammonia. The ordinate of Figure 2 exhibits the apparent densities of the product fibers, while the abscissa shows the atomic ratios of carbon atoms in the feedstock mixtures. Similar experiments were performed using mixtures with nitrogen substituted for ammonia. Finally, one experiment was performed using a 3:1 mixture of H_2 to N_2. It seems clear that for all gas mixtures the fibers produced with ammonia at a C/(H+N) ratio of 0.12-0.22 had the lowest apparent density and hence the highest quality.

Experiments in the horizontal system at 13 cm^3/min of H_2S, 137 cm^3/min of He bubbled through $Fe(CO)_5$, and 6,000 cm^3/min of various mixtures of methane and ammonia are also plotted in Figure 2. They confirm the superiority of the ammonia mixtures observed with the vertical reactor.

Further experiments were performed to compare the effect of several diluents on the fiber quality. Each experiment was performed at 1100°C, a methane flow rate of 10,300 cm^3/min, a He/$Fe(CO)_5$ flow rate of 384 cm^3/min, and a H_2S flow of 19 cm^3/min. The SEM photos of Figure 3 compare the material produced using the above mixture with the material produced by adding either NH_3, He, N_2, or a 3:1 mixture of H_2 and N_2, all flowing at 3,700 cm^3/min. There is a clear qualitative superiority in fiber length, straightness, and absence of soot in the fibers grown with an ammonia atmosphere We have confirmed in many other experiments [4] that this method produces the highest quality fibers. In one statistical tabulation, ammonia addition increased average fiber length from 11 to 43 μm.

DISCUSSION

Previous work has shown that diluting the fiber growing hydrocarbon mixture [5] increases the length of the fibers while decreasing the number of fibers produced. However, the increase in length and straightness observed here is better with ammonia than with either nitrogen, helium, or nitrogen/hydrogen mixtures.

The well known ability of ammonia to nitride iron in this temperature and concentration range [6] suggests that N atoms are dissolving in the catalyst particles. It may well be that nitrided Fe particles or droplets have a superior ability to nucleate fiber growth and that this enhanced growth competes successfully in the gas phase with soot formation.

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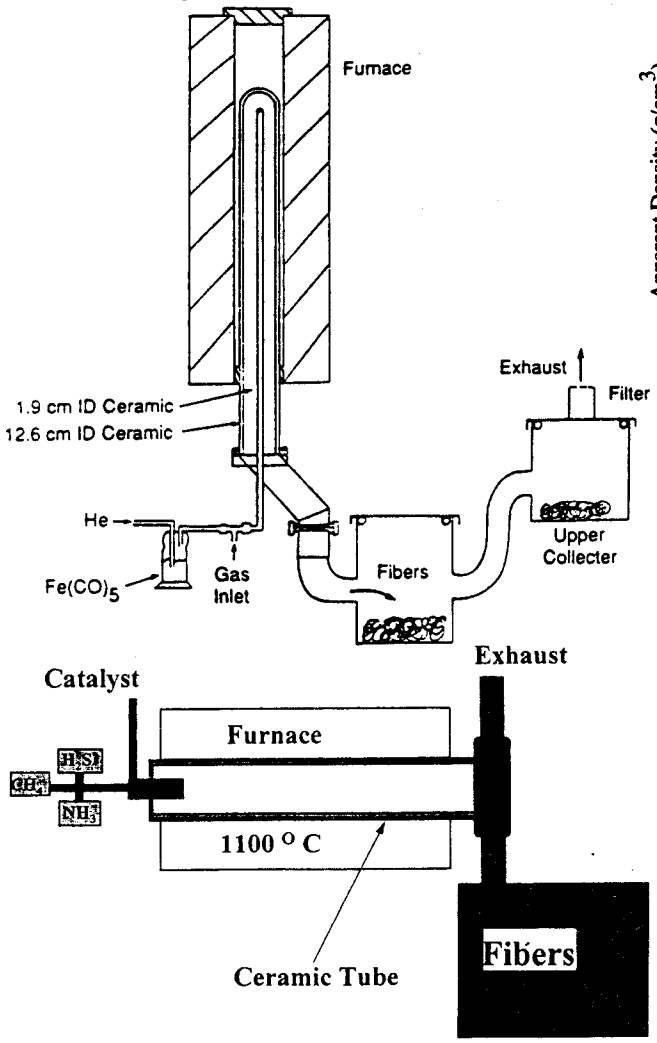

Figure 1. The top panel shows the vertical reactor with a 1.9 cm ID injector inserted 89 cm into the 12.6 cm ID tube of heated length 95 cm. The bottom panel shows the horizontal apparatus whose injector is a 2 cm ID tube inserted 30 cm into a 10 cm ID tube of heated length 183 cm. All tubes are of mullite.

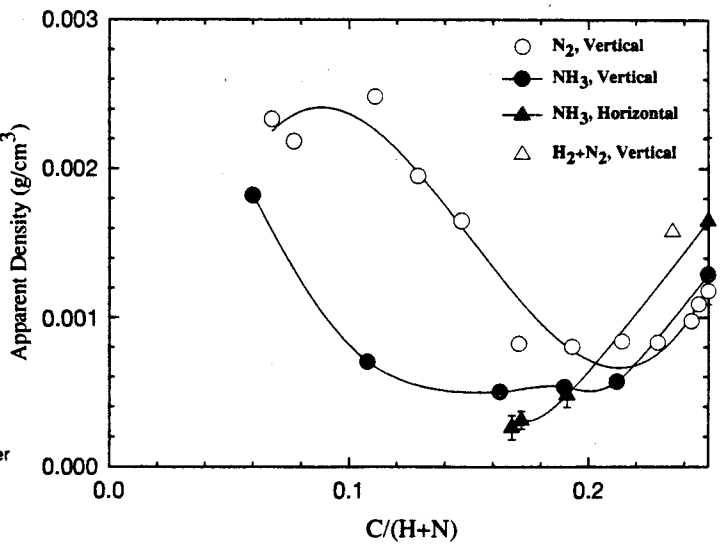

Figure 2. Apparent densities of fibers grown with 6 cm^3/min of H_2S, 155 cm^3/min of He bubbled through $Fe(CO)_5$, and 6600 cm^3/min of various mixtures of methane diluted with either ammonia (filled circles), or nitrogen (open circles). The total flow rate for the data point using 1:3 nitrogen:hydrogen diluent was 5,600 cm^3/min. Results from the horizontal system at 13 cm^3/min of H_2S, 137 cm^3/min of He bubbled through $Fe(CO)_5$, and 6,000 cm^3/min of various mixtures of methane and ammonia are plotted as filled triangles. The abscissa represents the dilution of the methane and ranges from 0 to 100% methane.

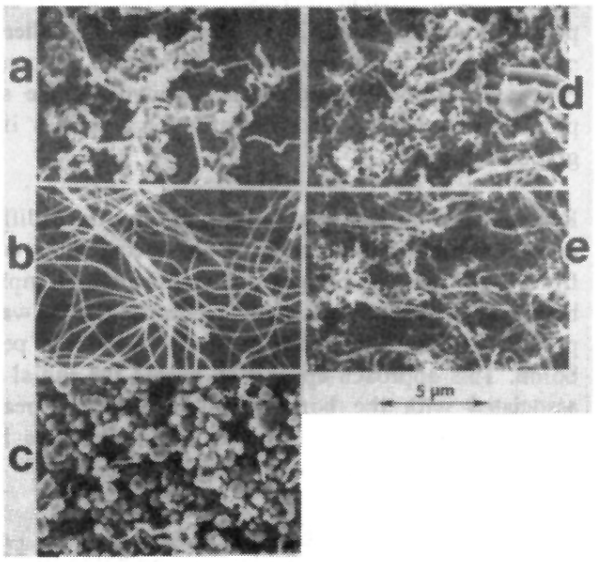

Figure 3. (RIGHT): a) SEM photos of fibers grown in the horizontal reactor with 19 cm^3/min of H_2S, 384 cm^3/min of He bubbled through $Fe(CO)_5$, and 10,300 cm^3/min of methane. Fibers grown with the above mixture plus 3,700 cm^3/min added b) ammonia c) helium, d) nitrogen, e) hydrogen:nitrogen in a 3:1 ratio.