CO_2 MIXING EFFECT ON PREPARATION OF FE-CATALYZED CARBON NANOFIBERS

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Introduction

Carbon nanofibers (CNFs) have been recognized as unique forms of carbon materials that are produced by the decomposition of selected hydrocarbons over metal particles [1-4]. These quasi-one dimension materials are formed by the piling up of graphite layers along the fiber axis as a vertical, perpendicular, or angled form, offering different well-controlled surface, such as basal and edge surfaces. Therefore, CNFs can not only regard as ideal materials with identified surface for fundamental researches, but also have wide potential applications in chemical sensing, adsorption, thermal protection, battery electrode, especially in catalyst support [5-8].

To prepare CNFs using exhausted gases from industries is considered to be the most effective route to realize the CNF production with inexpensive supply. In generally, the exhausted gases contain various hydrocarbons, such as ca. 20% CH_4, 30% C_2H_4, 15% C_3H_6, and 24% CO, which can be used as carbon feedstock to produce CNFs. However, there are also some potential oxidizing gases for the produced CNFs, e. g. ca. 8% CO_2 remained in the exhausted gases. In this work, we investigated influence of co-existence of CO_2 on catalytic CNF growth using C_2H_4 as a carbon source over unsupported and MgO-supported iron particles. It was found that variation of CO_2 concentration resulted in significant changes in both CNF yield and its morphologies.

Experimental

The unsupported Fe nanoparticles were prepared by the precipitation of iron carbonates from the corresponding nitrate solution using ammonium bicarbonate in prescribed amounts. The MgO-supported iron catalysts (FM11, the mass ratio of Fe to MgO was 1/1) were prepared by the same precipitation approach using the magnesium and iron nitrates as starting materials. The obtained carbonates were calcined at 400 ^oC for 6 h into oxides. The oxides were reduced at 500 ^oC for 20 h under hydrogen and helium atmosphere (H_2/He=1/9 (vol/vol)), followed by passivation process under 10% air atmosphere at room temperature.

CNFs were prepared in a quartz flow reactor (10 cm (D), 45 cm (L)) heated by a conventional horizontal tube furnace. The gas flow to the reactor were precisely monitored and regulated by mass flow controllers. Powered catalysts (30 mg) were placed in a quartz tray at the centre of the reactor tube. After reduction in a 20% H_2/He mixture for 2 h at a prescribed reaction temperature, helium was flushed for 30 min before an introduction of the $C_2H_4/H_2/CO_2$ mixture (total flow rate 200 ml/min). The CNF growth time was set at 1 h.

The total carbon conversion was described gravimetrically as the weight of products per the exhausted total carbon content from C_2H_4. The structure of produced CNFs was examined using field emission scanning electron microscope (SEM; JSM-6320F, JEOL). For SEM observation, a powdered sample was well dispersed over a piece of carbon tape sticking to a cylindrical sample holder of copper.

Results and Discussion

Fig. 1 illustrates the total carbon conversion of C_2H_4 over unsupported and supported Fe catalysts at CO_2 concentration between 0% and 80%. In absence of CO_2, C_2H_4 was hardly catalytically converted into solid carbons over Fe catalysts regardless of MgO support. The CO_2 addition caused an immediate increase in the total carbon conversion. Such increase was more significant for higher temperature or unsupported catalysts. Further increasing the CO_2 concentration to 80%, deactivation was observed for all samples. This result indicates that CO_2 could facilitate the decomposition of C_2H_4 and/or catalytic performance of Fe catalysts, and thus the growth of CNFs in the relative wide concentration range (at least 0-50%).

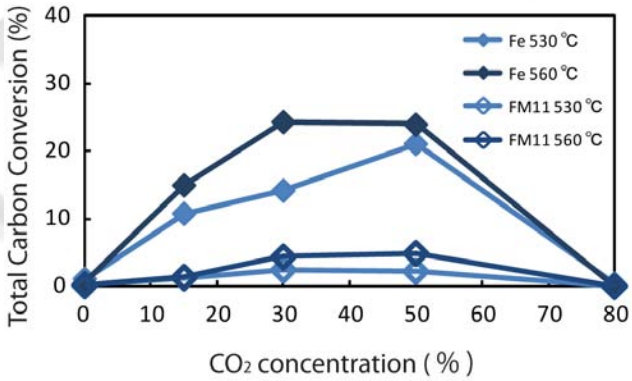

Fig. 1 Total carbon conversion at CO_2 concentration between 0% and 80% for unsupported or MgO-supported Fe catalysts at 530 ^oC and 560 ^oC

The morphologies of as-prepared products over unsupported and MgO-supported Fe catalysts at 560 ^oC are shown in Figs. 2 and 3, respectively. For unsupported Fe catalyst, in the absence of CO_2, the product was granular form, suggesting that the catalysts are easily encapsulated by the deposited carbon films, resulting in very low carbon conversion. The CO_2 addition caused the formation of filamentous carbons. These carbon fibers had smooth surface and relative larger diameter of ca. 100-200 nm. The length of fibers was as long as hundreds of micrometer or even beyond, suggesting that the Fe catalysts have very high activity in the presence of CO_2. The diameter of the products seemed to decrease with the increase of CO_2 concentration. For MgO-

supported Fe catalyst, on the other hand, even in the absence of CO_2, very thin carbon nanofibers were obtained, although the yield was not high. This should be attributed to high-dispersion effect of the Fe catalyst on the MgO support. Interestingly, the CO_2 addition seemed to diminish the supporting effect by MgO support, and only thick carbon nanofibers were obtained.

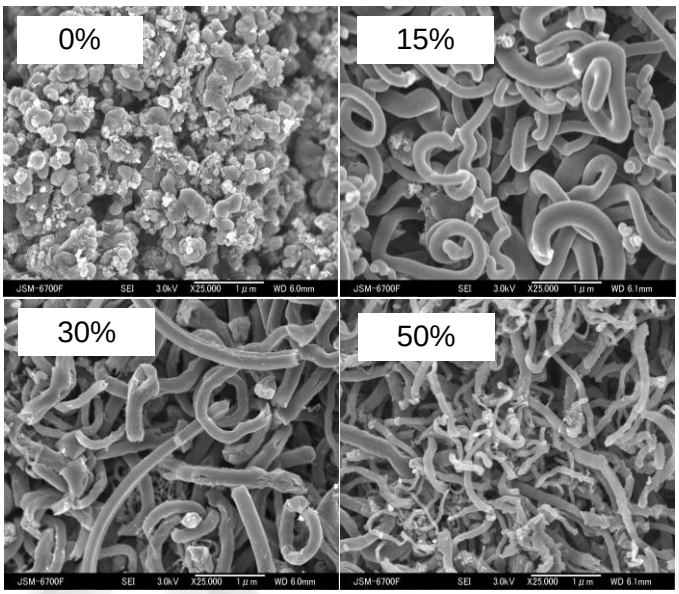

Fig. 2 SEM images of as-prepared products at different CO_2 concentrations operated at 560 ^{o}C over unsupported Fe catalyst.

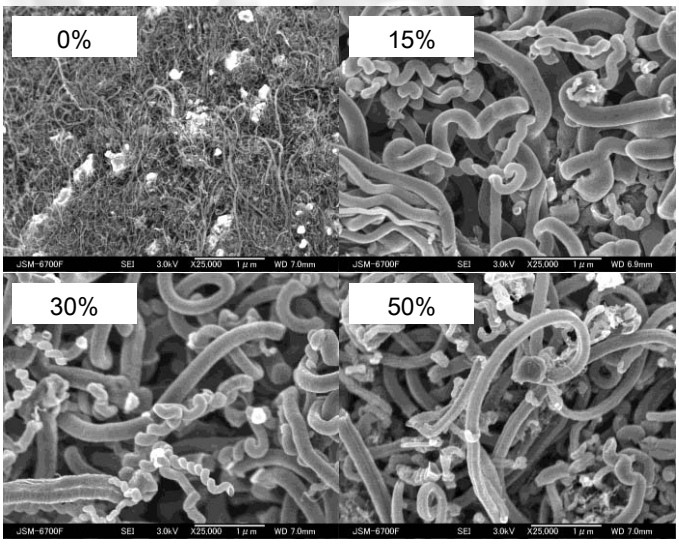

Fig. 3 SEM images of as-prepared products at different CO_2 concentrations operated at 560 ^{o}C over MgO-supported Fe catalyst.

Fig. 4 presents the total carbon conversion over unsupported catalysts at different growth temperatures in the presence of 50% CO_2. At the low temperatures (< 470 ^{o}C), no carbons were deposited on the Fe catalysts. When the temperature rose to 470 ^{o}C, very low carbon conversion, only about 1% was observed. Further increasing the temperature to 500 ^{o}C, the conversion increased to 5%, and then remarkably increased to 22% at 530 ^{o}C of the growth temperature, and kept this level at the temperature range of 530-590 ^{o}C. The total carbon conversion decreased significantly with the further increase of temperature and then to zero at the temperature of 650 ^{o}C. This result suggests that the growth of CNFs in the presence of CO_2 is only available at the moderate temperature (e.g. 530-590 ^{o}C).

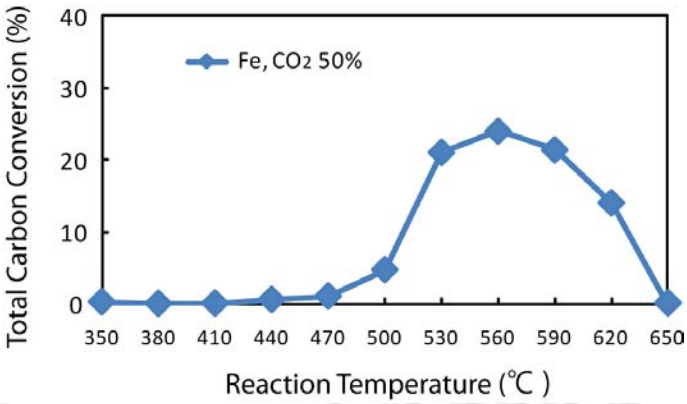

Fig. 4 Total carbon conversion at 50 % of CO_2 concentration using Fe catalyst at different growth temperatures

Conclusions

We found that carbon nanofibers can be grown on Fe catalysts by decomposing C_2H_4 even in the presences of CO_2 at a relative wide concentration range. Addition of CO_2 induced the increase of total carbon conversion and influenced on morphology of CNFs. A mechanism of the improved carbon nanofiber growth with the CO_2 addition is now under investigation.

References

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