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Carbon Nanotube Formation Over Supported Catalysts

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Catalytic synthesis and characterization of multi-wall fullerene nanotubes are presented. Supported transition metal catalysts were prepared by different methods and were tested in the decomposition of hydrocarbons. Reactions were carried out in a fixed bed flow reactor at 700°C at atmospheric pressure. Both activity and selectivity of catalyst samples depended mainly on the following parameters: catalyst support, transition metal, initial reactant, and reaction temperature. The quality of the product was characterized by TEM. Although the ends of these catalytically produced carbon nanotubes are often closed by fullerenic half-onions, they can be opened with ease in a relatively gentle liquid-phase oxidation procedure. Neither drastic purification process with HF nor oxidative treatment destroyed the quality of the tubes. IR and XPS investigations confirmed that carbon nanotubes having inner diameter larger than 1-2 nm show graphitic feature.

Keywords: carbon nanotubes; catalytic synthesis; purified nanotubes

INTRODUCTION

Different forms of carbon materials provide a great variety of nanostructures. After the discovery of fullerenes, much attention was paid to the production and investigation of carbon nanotubes[1-3]. In addition to their predicted chemical and physical properties[4,5], this quasi one-dimensional carbon system can be a unique graphite-like host for intercalation of com-

pounds. Carbon nanotubes were filled with molten lead through capillary action[6]. Capillarity and wetting of carbon nanotubes were studied by Dujardin et al. in detail[7]. Indirect method was used for the filling of carbon nanotubes with long continuous MoO_2 crystals[8] Successful intercalation into carbon nanotubes without breaking the tubular structure was observed by Mordkovich[9].

EXPERIMENTAL

Supported transition metal catalysts were prepared by impregnation or ion-adsorption precipitation method using Co- or Fe-acetate solution and silica (zeolite) as catalyst support. Synthesis was carried out in a fixed-bed flow reactor in the temperature range of 700-800°C. The gas feed was 10 % acetylene diluted with nitrogen and the average contact time was 15 seconds. The quality of the carbon deposit on the catalyst surface was investigated by TEM (Philips XL 20). Purification of zeolite supported sample was carried out in two steps: dissolution of catalyst particles in HF and oxidation of amorphous carbon by acidic $KMnO_4$ solution[10]. Purified carbon nanotubes were investigated by infrared and Raman spectroscopy. Further details of experimental is given elsewhere[11-14].

RESULTS AND DISCUSSION

Catalyst Preparation

Supported cobalt and iron were found to be active in the decomposition of acetylene. Oxygen-containing materials (such as silica or zeolite) proved to be suitable as catalyst support. Co or Fe oxide without any preliminary reduction provides precursor of active sites on the surface. According to ESCA investigations, catalytically active sites form *in situ* at the beginning

of the reaction and contain partially reduced Co or Fe oxide particles. Neutralization of catalyst sample during preparation increased selectivity of carbon nanotube formation significantly. Slight alkaline pH of solution promotes formation of spiral nanotubes.

Synthesis of Nanotubes

Carbon nanotubes were synthesized in the decomposition of acetylene (or other carbon-containing compounds such as ethylene, propylene, pentane, acetone, etc.) over supported Co or Fe catalyst samples. Catalytic preparation can produce carbon nanotubes with very high selectivity (regular nanotubes/total carbon deposit) under relatively mild conditions. The

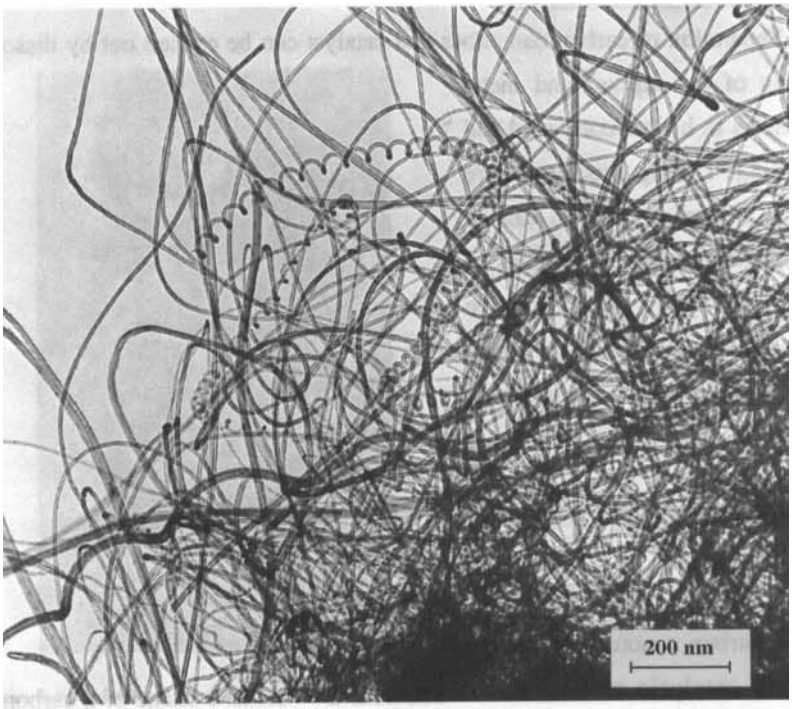

FIGURE 1 Carbon nanotubes on the surface of Co/silica

optimum reaction temperature was found to be 700-770°C depending on initial reactant. Figure 1 shows carbon nanotubes obtained in the decomposition of acetylene over Co/silica at 700°C. In the case of acetylene, decreasing temperature results in lower yield and poorer quality of graphitization but increasing reaction temperature is favorable for homogeneous decomposition of acetylene thus formation of amorphous carbon.

While iron was the most active transition metal in the decomposition of compounds, cobalt samples produced carbon nanotubes of better quality, of perfect graphitization. Although silica-supported samples showed high activity, zeolite-supported catalysts have indisputable advantages during purification procedure.

Purification of the Samples

Separation of carbon nanotubes and catalyst can be carried out by dissolution of the support and metal particles in hydrofluoric acid and filtering. During this procedure some amorphous carbon can be liberated from the inner pores of catalyst support which can be selectively oxidized in liquid phase by acidic permanganate solution.

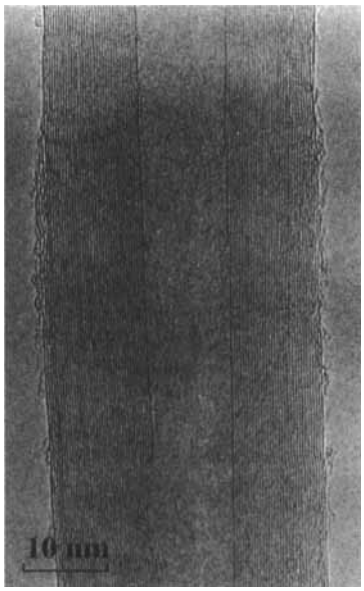

FIGURE 2 HREM image of a carbon nanotube

Characterization of the Nanotubes

According to TEM observations, carbon nanotubes prepared by the catalytic method have

regular structure. They are built up from concentric cylindrical graphene sheets with the characteristic interlayer distance of 3.4 Å. The inner diameter of the tubes varies from 5 to 15 nm depending on the nature of the catalyst and the initial reactant. Diameter depends on the size of metal particles dispersed on the surface of support[13,14], for e.g. carbon nanotubes obtained over Fe catalysts were thinner. HREM image of a nanotube can be seen on Fig. 2. The number of the layers of a multiwall tube can be up to one hundred. The ratio of length to diameter is at least one thousand. (30 min. reaction) According to theoretical calculations[15], multiwall carbon nanotubes having inner diameter larger than 1-2 nm show graphitic feature.

For the purified samples this was confirmed by Raman spectroscopic

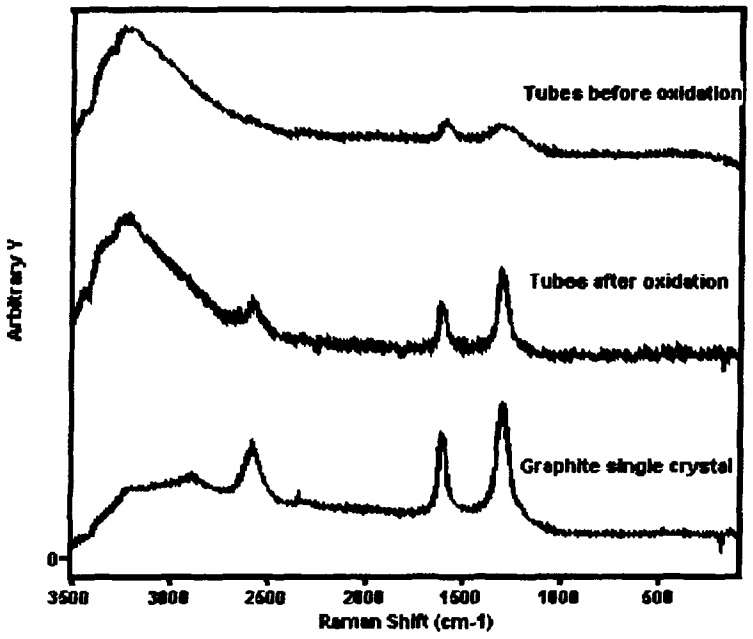

FIGURE 3 Raman spectra of carbon nanotubes at different stages of purification

investigations as it is illustrated on Fig. 3. Spectrum a was made of sample after HF and before oxidation treatment. Spectra b and c give comparison between purified carbon nanotubes and graphite.

Acknowledgements

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