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Flat interface mediated synthesis of platelet carbon nanofibers on Fe nanoparticles

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ABSTRACT

A novel approach to synthesize platelet carbon nanofibers (PCNFs) is proposed by taking advantage of the flat interfaces between Fe nanoparticles and flake supports. PCNFs are produced when Fe nanoparticles are supported on flakes of mica, SiO_2 and graphite, and only fishbone carbon nanofibers (FCNFs) are obtained when γ-Al_2O_3 is used as a support. The crystalline perfection of PCNFs is found to depend on the dispersion of the catalyst and the surface roughness of the support. Perfect PCNFs are obtained when mica, which has a high surface tension and a very flat surface, is used as a support. The yield of PCNFs changes little with the nature of the support but is strongly related to the size of Fe nanoparticles and the preparation method of the Fe catalysts.

1. Introduction

Carbon nanofibers (CNFs) have aroused extensive interests in catalysis owing to their unique physico-chemical properties. In addition to their high chemical and thermal stability and strong mechanical strength, the possibility of tuning the arrangement of surface carbon atoms and introducing on-purpose some oxygen or nitrogen containing groups makes the CNFs very attractive in both fundamental studies in catalysis and applications in various of chemical and electrochemical reactions [1–9]. Moreover, thanks to the fibrous structure, the surface of the CNFs is easily accessible for reactants, which makes it possible to alleviate or eliminate the diffusion resistance. Among all the fibrous nanocarbon materials, the platelet carbon nanofibers, which have a large amount of less coordinated edge atoms, are particularly good supports and catalysts [2–4].

Catalytic chemical vapor deposition (CCVD) on transition metal catalysts is the prevalent pathway for CNF growth, and the mechanism of CNF growth over transition metal catalysts, such as Fe, Ni, and Co, has been extensively studied. It involves sequentially carbon atom formation on metal surface, dissolution into the subsurface of the metal, diffusion on the surface or into the bulk of the metal, and segregation to form graphene layers [5–8]. Carbon nanofibers of various structures may be formed, depending primarily on the nature and shape of the catalyst particle and orientation of the precipitating faces [5,6]. During CNF growth, the nature of the catalyst can be changed by surface and subsurface carbon atoms, and the shape and orientation of the particle faces will be changed with reacting conditions, i.e. the atmosphere and temperature for reaction. In addition, the size and hence the shape of the catalyst will also change during CNF growth. All this complicates the mechanism of CNF growth and makes the controlled growth of CNF with defined morphological characteristics difficult.

While it is relatively easy to control the diameter of the carbon nanofibers by adjusting the size of the metal nanoparticles, for example, by changing the metal loading, or using different catalyst preparation procedures, it still remains a big challenge in production of the high-purity PCNFs. In this work, we propose for the first time to use flakes as the support for metal nanoparticles to produce straight and less entangled PCNFs. Because of the flat interfaces between the metal nanoparticles and the flake supports, all the metal nanoparticles have a flat facet. Moreover, carbon may preferentially nucleate at the interface to form an initial flat graphene sheet, which acts as the template for upcoming carbon atoms to produce a PCNF [5,6]. The merit of this approach is demonstrated by the synthesis of PCNFs with iron nanoparticles supported on various flakes such as mica, silica, and graphite. As a comparison, iron nanoparticles supported on alumina powder are also used for CNF growth under the same reaction conditions, which produce only FCNFs.

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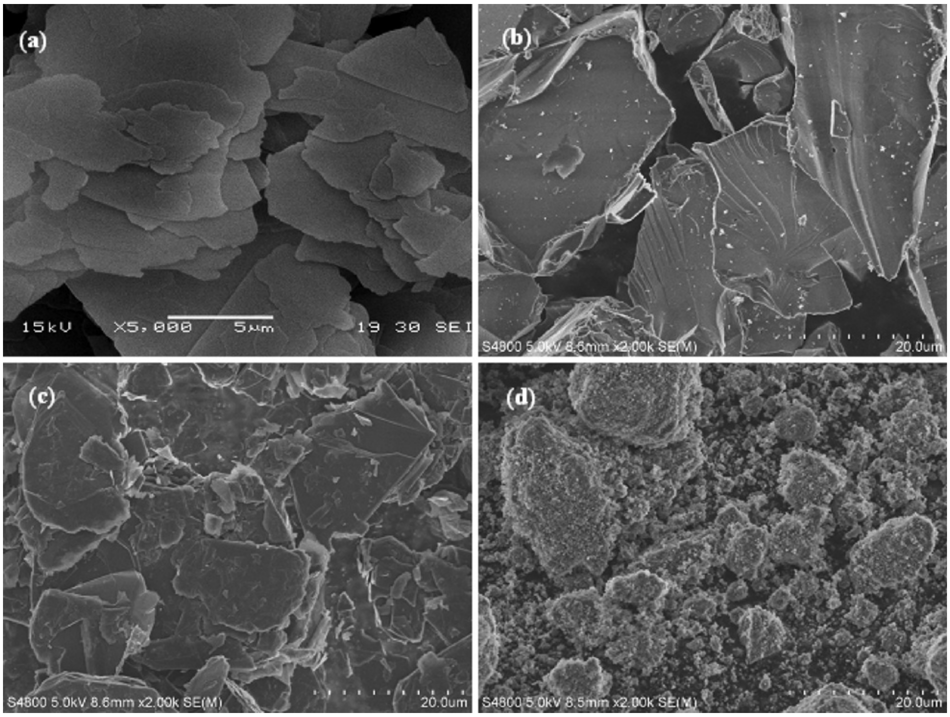

Fig. 1. SEM image of mica (a) and FESEM images of silica (b), graphite (c) and γ-Al_2O_3 (d).

2. Experimental

2.1. Preparation of Fe catalysts and synthesis of CNFs

Mica, silica and graphite flakes and γ-Al_2O_3 powder were used as catalyst support. The catalysts containing 0.5–10.0 wt% Fe with different supports (mica, silica, graphite, and γ-Al_2O_3) were prepared by incipient wetness impregnation (IWI) with an aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$, while the catalysts containing 20.0 wt% Fe were prepared by deposition–precipitation (DP) of $Fe(OH)_3$ at pH 5.0 and ambient temperature for 12 h. The DP procedure was similar to that described in the literature [3,10]. All the catalysts were dried in stagnant air at ambient temperature for 12 h, at 120 °C for 12 h and calcinated in air at 600 °C for 3 h in an oven, and activated at 600 °C for 3 h in a flowing Ar/H_2 mixture (120/40 mL/min). A mixture of CO/H_2 (160/40 mL/min) was then introduced to the catalysts for CNFs synthesis for 2 h in a fixed bed reactor. The as-synthesized CNFs were characterized by thermal gravimetric analysis (TGA) in 100 mL/min air at 800 °C for 4 h [4]. From the weight of the remained solids, the carbon yield (g/g_{cat} or g/g_{Fe}) was calculated.

2.2. Catalyst characterization

The microstructure and the morphology of supports were characterized by scanning electron microscopy (SEM, JOEL JSM 3360LV, Japan) and field emission scanning electron microscopy (FESEM, S-4800 UHR). The microstructure and the morphology of Fe catalysts and CNFs were studied by a high-resolution transmission electron microscope (HRTEM, JOEL JEM-2100F) with an accelerating voltage of 200 kV and a point resolution of 0.19 nm. The catalyst powder was dispersed in ethanol, and the suspension was then dropped onto a holey carbon-coated copper grid. The average size of Fe nanoparticles, whose shape was assumed to be spherical, was estimated based on the random sizes of 100 nanoparticles according to $d_n = \sum n_i d_i / \sum n_i$ [4], where d_i is the nanoparticle diameter measured from the HRTEM and n_i is the number of Fe nanoparticles. X-ray diffraction (XRD) was performed on a Rigaku D/Max 2550 VB/PC diffractometer using Cu Kα radiation. In addition, for the characterizations of the Fe/mica catalysts by TEM and XRD, the metal oxides were reduced to the metallic state in a mixture of Ar/H_2 (160/40 mL/min) for 3 h at 600 °C. After reduction, the Fe catalysts were cooled to room temperature in Ar flow and passivated in an O_2/Ar mixture (1 vol% O_2, 100 mL/min total flow) for 2 h to prevent bulk oxidation of the Fe nanoparticles. The textural properties of the supports and CNFs were characterized by N_2 physisorption on ASAP 2010C (Micromeritics, USA) at 77 K after out-gassing the samples at 190 °C and 1 mmHg for 6 h. The laser Raman spectra were performed in an inVia Raman microscope (Renishaw, UK).

3. Results and discussion

Fig. 1 shows that all the flakes have flat surfaces while the powders are porous, corresponding to the low surface areas of the flakes and the high surface area of the powder listed in Table 1. In addition, the mica surface is very smooth while those of silica and graphite are relatively rough. The properties of Fe catalysts including the Fe loadings and the nanoparticle sizes, and the microstructures of CNFs are shown in Table 1.

3.1. Effect of Fe nanoparticle size on the synthesis of PCNFs

The Fe nanoparticle sizes estimated based on XRD and HRTEM are presented in Table 1. There is no direct relationship between the support BET surface area and the Fe nanoparticle size. For porous powder support, such as γ-Al_2O_3, the surface area is mainly contributed by the micro/meso-pores and capillary effect plays the dominating role during impregnation. As a result the dispersion is strongly related to the surface area of the support. For flake support, the surface area is mainly contributed by the flat surface, as evidenced by the SEM shown in Fig. 1, and the dispersion is determined by the wettability of the surface. The liquid droplets containing the catalyst precursor cannot wet the graphite surface and can easily migrate and coalesce to form particles with large size and distribution. However, the liquid can easily wet the mica