Article ID: 1007-8827(2012)02-0153-04

A high strength carbon nanofiber/honeycomb cordierite composite produced by chemical vapor deposition

WANG Yan-li, WANG Xu-jian, ZHAN Liang, QIAO Wen-ming, LIANG Xiao-yi, LING Li-cheng

(*State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai* 200237, *China*)

Abstract: A carbon nanofiber (CNF)/honeycomb cordierite composite with a compressive strength of 50 MPa was prepared by chemical vapor deposition, using C_2H_4 as the carbon source and Ni-Cu alloy as the catalyst. The CNFs with a diameter of 20-30 nm in the cells of the honeycomb interweave with each other to form a 5 μm- thick layer. The CNF content is 25.3 wt%. The Cu has remarkable effects on the particle size of the Ni-Cu alloy, which further affects the growth rate, loading level and nanostructures of the CNFs. The CNFs are not well graphitized and the insertion of the CNFs into the honeycomb can increase its compressive strength from 10 to 50 MPa.

Keywords: Carbon nanofibers; Ceramic monolith; Microstructure; Defects

CLC number: TB 332 **Document code**: A

1 Introduction

In the last decade, carbon nanofibers (CNFs) were extensively studied especially for their use as catalyst support. Compared with traditional catalyst supports, CNFs display high activity and peculiar selectivity due to the one-dimensional (1D) nanostructures, absence of micropores, abundant graphene edge sites and high thermal conductivity[1-3]. Recently, Su et al[4]. have found that when carbon nanomaterial (e. g. CNFs) is used directly as the catalyst for catalytic dehydrogenations reactions, it exhibits an outstanding catalytic activities because of the C═O bond. The graphene arrangement of CNFs has been found to have great effect on the 1D nanostructures, graphene edge sites and surface chemistry, and therefore on the catalytic activity in heterogeneous catalysis[5]. Baker investigated the influence of CNF microstructures on supported Pt, Cu and Ni particles and found that the atomic arrangement of active particles is dictated by the graphene arrangement and hence plays an important role in their activities[6]. Zhao reported that a larger amount of oxygen-containing groups, such as carboxyl, was strongly dependent on the graphene arrangement of CNFs[7]. Therefore, how to control the graphene arrangement of CNFs is crucial to their catalytic performance.

Owing to the powder form, CNFs suffer from their high mass transfer resistance to liquid-phase catalytic reactions and are difficult to be used directly in fixed-bed reactors because of a high pressure drop. So it is of great importance to find out new methods to synthesize CNFs with a formed shape for a subsequent use as catalyst support or catalyst. Currently, many types of porous carbons, foams and monoliths have been reported as substrates for CNF growth[8-9]. It is noteworthy that the macroscopic shape of CNF/substrate composites should have a high mechanical strength to avoid breaking and catalytic bed plugging, have high specific surface area to disperse metal catalyst or to afford abundant active sites, and have a low flow resistance in order to be used under aggressive flow. Among them, ceramic monoliths may be the most promising candidates to satisfy the engineering requirements.

The aim of this article is to study the synthesis of thin CNFs on ceramic monoliths by using Ni-Cu alloy as the catalyst and C_2H_4 as the carbon source. The effects of the Ni-Cu alloy on the nanostructures and the yield of CNFs were discussed.

Received date: 2011-09-30; **Revised date**: 2012-02-20

Foundation item: National Natural Science Foundation of China (20806024, 51002051, 50730003, 50672025 and 20977028), Fundamental Research Funds for the Central Universities (WA1014016), Research Fund for the Doctoral Program of Higher Education of China (20090074110009) and Research Fund of China 863 Program (2008AA062302).

Corresponding author: ZHAN Liang. Tel: +86-21-64252924; Fax: +86-21-64252914, E-mail: zhanliang@ecust.edu.cn

Author introduction: WANG Yan-li (1975-), female, Ph. D., Associate Professor. engaged in the nano-carbon materials.

English edition available online ScienceDirect (http://www.sciencedirect.com/science/journal/18725805).

DOI: 10.1016/S1872-5805(12)60009-2

2 Experimental

2.1 Catalyst preparation

The ceramic monolith (2 cm in diameter, 5 cm in length, 200 cells per square inch) was coated with an alumina layer by the sol-gel dip-coating method. The monolith was impregnated with a solution mixture of nickel nitrate and copper nitrate to give a nickel oxide loading mass fraction of about 0.5% and a Ni/Cu atomic ratio of 6∶1, and dried at 50 ℃ and then 110 ℃ for 8 h. Finally, the dried monolith was calcined at 600 ℃ for 2 h. For comparison, the monolith-supported NiO sample, with a NiO loading of 0.5% by mass fraction, was also prepared using the same method.

2.2 Synthesis of CNFs on ceramic monolith

The alumina-coated ceramic monolith was placed in a horizontal quartz reactor. Initially, the monolith was reduced with H_2/He mixture (H_2, 20% by volume fraction) at 600 ℃ for 2 h. Then, when the monolith was heated up to the growth temperature (500-750 ℃), the gas was switched to C_2H_4/H_2 mixture with a C_2H_4∶H_2 volumetric ratio of 160∶40 at a flow rate of 200 mL/min. The CNF growth was stopped after a certain time, and the CNF/ceramic monolith composite was obtained.

2.3 Characterization

Scanning electron microscopy (SEM) of as-synthesized samples was carried out using a FEI Quanta 200FEG operated at 5 kV. Transmission electron microscopy (TEM) was carried out on a JEOL 2010F operated at 200 kV. And the porous characterization was performed by the nitrogen adsorption/desorption isotherms at 77 K, using an automatic adsorption apparatus (ASAP2020, Micromeritics). The specific surface area of the samples was determined using the standard Brunauer-Emmett-Teller (BET) method. The compressive strength of the samples was determined by a universal material testing machine (Instron 1185).

3 Results and discussion

Fig. 1a presents the morphology of the CNF/ceramic monolith prepared at 700 ℃ for 120 min. The thickness of the CNF layer is about 5 μm and the opening pore structure of the ceramic monolith is kept unchanged. The strong attachment of the nanofibers, one of the characteristic features of the composite, is afforded by the deep-rooted CNFs in the alumina-coated layer. As can be observed from Fig. 1b, the synthesized CNFs with diameters of 20-30 nm interweave one another, forming some mesopores and macropores. The Ni-Cu alloy cannot be observed from the tips of the CNFs, suggesting that the CNFs are formed by the base growth mechanisms. The TEM image (Fig. 2a) indicates that the synthesized CNFs are of tubular type with the graphitic planes parallel to the fiber axis, and the thickness of the tube walls is about 10 nm. Another feature of the CNFs is that there are some knots along the axis. The high resolution TEM (Fig. 2b) shows that the graphite layers are not well developed and many defects can be observed among the layers, indicating that there are abundant graphene edge sites in CNFs.

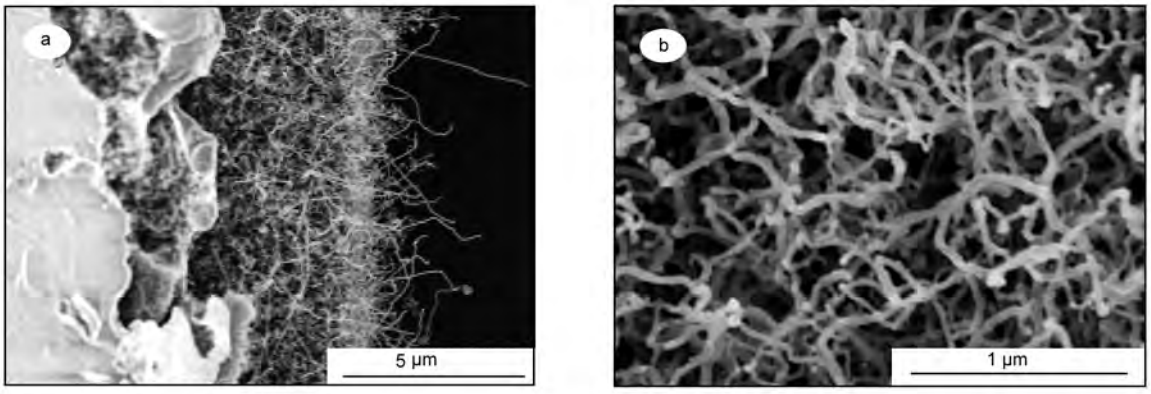

Fig. 1 SEM images of CNFs synthesized at 700 ℃ for 120 min

Fig. 3a presents the yields of CNFs with the growth time of 30 min at different growth temperatures. Compared with individual Ni catalyst, the Ni-Cu alloy is inactive in decomposing hydrocarbons at low temperatures (500-600 ℃), but it becomes active at high temperatures of 600-750 ℃. This suggests that the growth temperature plays an important role in CNF growth. The yields of CNFs prepared using a Ni-Cu alloy catalyst gradually increases with the growth temperature , probably because high

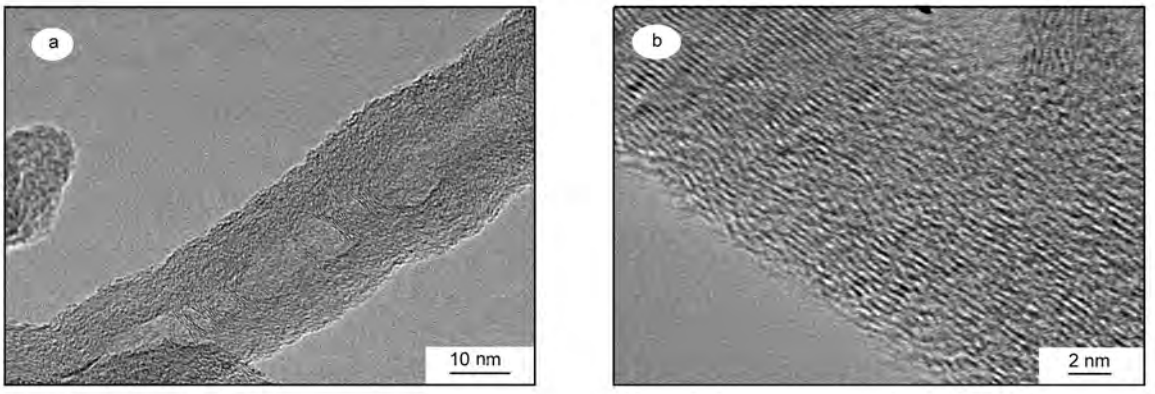

Fig. 2 (a) TEM and (b) high-resolution TEM images of CNFs synthesized at 700 ℃ for 120 min

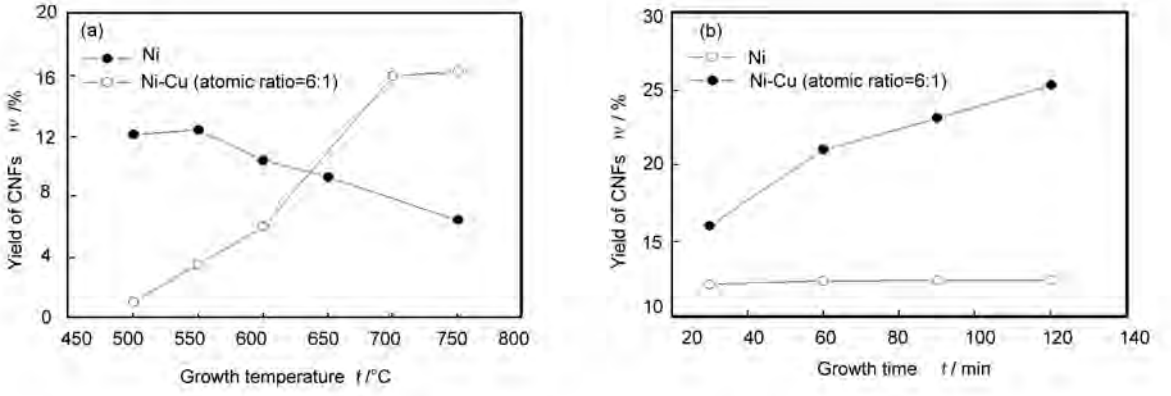

Fig. 3 Relationships between (a) the growth temperature, (b) growth time and the yield of synthesized CNFs

temperature easily results in sintering of the Ni catalyst particles and carbonaceous products are deposited on the surface of the Ni catalyst, leading to an activity loss of the Ni catalyst in the temperature range 600-750 ℃. It can also be deduced that the addition of Cu into Ni significantly raises the activity temperature of the Ni-Cu catalyst and thus improves its catalytic activity for CNF growth at high temperatures.

Fig. 3b shows the yield of CNFs as a function of growth time over individual Ni and Ni-Cu alloy catalysts. At a growth temperature of 700 ℃, the yield of CNFs prepared using Ni-Cu alloy catalyst increases with the growth time (Fig. 3b). When the growth time is 120 min, the yield of CNFs is 25.3% by mass fraction. However, in the time range from 30 min to 120 min, the yield of CNFs obtained from Ni catalysts at 550 ℃ does not change, which is around 12% by mass fraction. The BET surface areas of the CNF/ceramic monolith prepared using Ni-Cu alloy catalyst at 700 ℃ for 120 min and Ni catalyst at 550 ℃ are 58.2 and 37.6 m^2/g, respectively. However, it is worth noting that the BET surface area of the Al_2O_3-coated ceramic is only 9.2 m^2/g. It is therefore deduced that pores are formed during the CNF growth . The

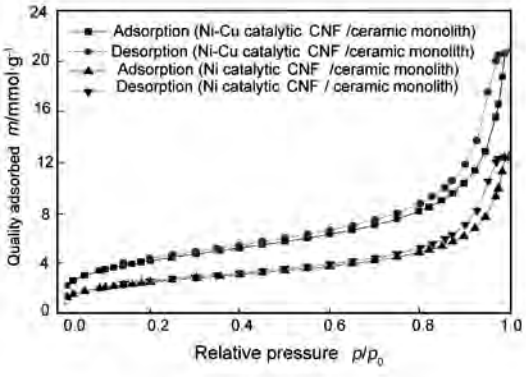

Fig. 4 Nitrogen adsorption/isotherms of CNF/ceramic monoliths

hysteresis loop between adsorption and desorption branch at $p/p_0 = 0.45$ and the almost vertical tail at p/p_0 near 1.0 (Fig. 4) reveal the presence of mesopores and macropores, which agree well with the results as discussed in Fig. 1b. Additionally, the original ceramic and the Al_2O_3-coated one exhibit a compressive strength of 10 and 11 MPa, respectively. The compressive strength of the CNF/ceramic monolith obtained from Ni catalyst at 550 ℃ for 30 min and that of the monolith prepared from Ni-Cu alloy catalyst at

700 ℃ for 30 min are 34 and 15.6 MPa, respectively. Increasing the growth time at 700 ℃ results in an increase in the compressive strength of the CNF/ceramic monolith produced from Ni-Cu alloy catalyst from 32.4 MPa for 60 min to 50.0 MPa for 120 min. As can be seen, the compressive strength of the CNF/ceramic monolith increases roughly linearly with the CNFs yield, suggesting the importance of the contribution of CNFs to the compressive strength of monoliths.

4 Conclusions

When CNFs were grown using C_2H_4 as the carbon source and Ni-Cu alloy as the catalyst, a thin layer of CNFs around 5 μm in thickness can be synthesized on a ceramic monolith with a yield of 25.3% and a compressive strength of 50.0 MPa. The graphite layers of the synthesized CNFs are not well developed and many defects exist among the layers, which is advantageous as catalyst support. Compared with CNFs prepared using Ni catalyst, the addition of Cu into Ni can inhibit the growth of metal particles, which further improves the growth rate, yield and nanostructures of CNFs at high temperature.

Acknowledgments

We thank the National Natural Science Foundation of China (20806024, 51002051, 50730003, 50672025 and 20977028), Fundamental Research Funds for the Central Universities (WA1014016), Research Fund for the Doctoral Program of Higher Education of China (20090074110009) and Research Fund of China 863 program (2008AA062302) for financial support.

References

[1] Enrique G B, Ingvar K, Chen D, et al. Carbon nanofibers uniformly grown on γ-Alumina washcoated cordierite monoliths [J]. Adv Mater, 2006, 18: 1589-1592.

[2] Cebollada P A R, Enrique G B. Optimisation of physical properties of γ-alumina coating microreactors used for the growth of a carbon nanofiber layer[J]. Chem Eng J, 2009, 149(1-3): 447-454.

[3] Lucia M L, Sabino A, Enrique G B. Temperature-mediated control of the growth of an entangled carbon nanofiber layer on stainless steel micro-structured reactors[J]. Carbon, 2010, 48(7): 2047-2056.

[4] Zhang J, Liu X, Blume R, et al. Surface-modified carbon nanotubes catalyze oxidative dehydrogenation of n-Butane[J]. Science, 2008, 322(5898): 73-77.

[5] Yoon S H, Lim S Y, Hong S H, et al. A conceptual model for the structure of catalytically grown carbon nano-fibers[J]. Carbon, 2005, 43(9): 1828-1838.

[6] Baker R T K, Rodriguez N, Mastalir Á, et al. Platinum/graphite nanofiber catalysts of various structure: characterization and catalytic properties[J]. J Phys Chem B, 2004, 108(38): 14348-14355.

[7] Zhao T J, Kvande I, Yu Y D, et al. Synthesis of platelet carbon nanofiber/carbon felt composite on in situ generated Ni-Cu nanoparticles[J]. J Phys Chem C, 2011, 115(4): 1123-1133.

[8] Stemmet C P, Meeuwse M, van der Schaaf, et al. Gas-liquid mass transfer and axial dispersion in solid foam packings[J]. Chem Eng Sci, 2007, 62(18-20): 5444-5450.

[9] Chinthaginjala J K, Bitter J H, Lefferts L. Thin layer of carbon-nano-fibers (CNFs) as catalyst support for fast mass transfer in hydrogenation of nitrite[J]. Appl Catal A, 2010, 383(1-2): 24-32.

化学气相沉积法合成高强度纳米炭纤维/蜂窝堇青石复合材料

王艳莉, 王绪建, 詹 亮, 乔文明, 梁晓怿, 凌立成

(华东理工大学,化学工程国家重点实验室,上海 200237)

摘 要: 以 C_2H_4 为碳源、Ni-Cu 合金作催化剂,采用化学气相沉积法在蜂窝状堇青石表面生长纳米炭纤维(CNFs),获得压缩强度为 50.0 MPa 的纳米炭纤维/蜂窝堇青石复合材料。在堇青石表面蜂窝腔内生长的 CNFs 直径为 20 nm ~ 30 nm,CNFs 之间相互交织形成 5 μm 厚的纤维层 ,CNFs 的质量分数为 25.3%。金属 Cu 的掺杂对 Ni-Cu 合金的颗粒尺寸产生重要影响,进而影响 CNFs 的生长速率、纤维层厚度及其微结构。所合成 CNFs 的石墨化程度不高,在蜂窝堇青石中生长纳米炭纤维可以把其压缩强度从 10 MPa 增加到 50 MPa。

关键词: 纳米炭纤维;蜂窝状堇青石;微结构;缺陷

基金项目:国家自然科学基金(20806024,51002051,50730003, 50672025, 20977028),中央高校基本科研业务费专项资金(WA1014016),高等学校博士学科点专项科研基金(20090074110009)和国家 863 重点项目(2008AA062302).

通讯作者:詹 亮. Tel: +86-21-64252924, Fax: +86-21-64252914, E-mail: zhanliang@ecust.edu.cn

作者介绍:王艳莉(1975-),女,陕西西乡人,博士,副教授,主要从事纳米材料的应用基础研究.