

Research Article

Catalytic Chemical Vapor Deposition of Methane to Carbon Nanotubes: Copper Promoted Effect of Ni/MgO Catalysts

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The Ni/MgO and Ni-Cu/MgO catalysts were prepared by sol-gel method and used as the catalysts for synthesis of carbon nanotubes by thermal chemical vapor deposition. The effect of Cu on the carbon yield and structure was investigated, and the effects of calcination temperature and reaction temperature were also investigated. The catalysts and synthesized carbon materials were characterized by temperature programmed reduction (TPR), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). Results showed that the addition of Cu promoted the reduction of nickel species, subsequently improving the growth and yield of CNTs. Meanwhile, CNTs were synthesized by the Ni/MgO and Ni-Cu/MgO catalysts with various calcination temperatures and reaction temperatures, and results suggested that the obtained CNTs on Ni-Cu/MgO catalyst with the calcination temperature of 500°C and the reaction temperature of 650°C were of the greatest yield and quantity of 927%.

1. Introduction

Due to the unique mechanical [1], chemical, electrical, magnetic, thermal, and other properties, carbon nanotubes (CNTs) have attracted many interests [1–3] and have been applied in various fields, such as electronics, medicine, and catalysis [3, 4]. Therefore, intense research efforts have been undertaken to produce CNTs at a reasonable cost. Currently, CNTs are mainly prepared by arc discharge [5, 6], laser evaporation [7], and chemical vapor deposition (CVD) methods [3, 8–11], among which the CVD method has been the most widely used method, appearing to be the most promising way to the large scale production of high purity CNTs at the lowest cost using the cheapest apparatus operating at a relatively low temperature [2].

In the CVD method, the quality and yield of CNTs are closely related to the used catalysts, reaction conditions, and the carbon source. In CVD synthesis of CNTs, Fe [12], Co [11, 12], and Ni [1, 8, 13, 14] as the active component on the oxides, such as Al₂O₃ [1], SiO₂ [15, 16], and MgO [8, 9, 12, 14, 17], or as an organometallic catalyst [16, 18], is usually used as catalyst. In addition, methane [9, 12, 14],

acetylene [2], and other hydrocarbons compounds [10] or CO, CO₂ [4], ethanol [17], and the like [11, 16, 19] are usually used as the carbon source.

According to the literature [14, 20, 21], with preparing CNTs by the Ni/MgO catalyst, the NiO and MgO solid solution structure was easily formed and then reduced to very fine nickel particles when subjected to high temperature, subsequently producing the CNTs with narrow diameter, thin wall, and good quality. Since few Ni particles were reduced from the solid solution structure, only a small amount of CNTs was produced. Studies showed that the introduction of suitable additive in Ni/MgO catalyst can not only increase the amount of reduced Ni particles, but also prevent the formation of amorphous carbon and prolong the stability of the catalyst [17]. For 50% Ni/MgO catalyst (wt.%), the optimum content of copper (Cu) was 4~6% to obtain high yield and quality of CNTs. In this study, the CNTs were synthesized using Ni/MgO and Ni-Cu/MgO catalysts, and the effect of Cu on the carbon yield and structure were investigated, and the effects of calcination temperature and reaction temperature were also investigated.

TABLE I: Prepared conditions of the catalysts.

Catalyst	Ni (wt.%)	Cu (wt.%)	Calcination temperature (°C)	Reaction temperature (°C)
Ni/MgO	50	0	400~500	550~750
Ni-Cu/MgO	50	5		

2. Experiment

2.1. Preparation of Catalysts. The catalysts Ni/MgO and Ni-Cu/MgO were prepared by sol-gel method, and the prepared conditions of the catalysts were shown in Table I. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and citric acid with a stoichiometric ratio were dissolved in deionized water, subsequently stirring and evaporating at 70°C until the solution became viscous colloids. Then the catalysts were dried in an oven at 120°C for 24 h and placed in the muffle furnace calcined at 400~500°C for 3 h.

2.2. Experimental Procedure. 100 mg of the catalyst powder was dispersed on a ceramic boat and then placed in a horizontal quartz reactor (inner diameter = 3.5 cm) to grow CNTs. Firstly, the catalyst powder was reduced in situ in H_2 at 550°C for 1 h and then raised to the reaction temperature of 550~750°C. Subsequently, the system was switched to methane of high purity (50 mL/min) for 1 h. After the reaction, the as-grown CNTs were cooled to room temperature in N_2 atmosphere.

2.3. Characterization. The catalysts and produced CNTs were characterized by means of hydrogen temperature-programmed reduction (H_2 -TPR), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA).

3. Results and Discussion

Temperature programmed reduction of H_2 (H_2 -TPR) is usually employed for estimating reducibility of the catalyst. The H_2 -TPR profiles of Ni/MgO with various calcination temperatures were displayed in Figure 1. The catalysts presented two reduction peaks; one centered at 300°C and the other broad peak existed at around 645°C or so. Most of the nickel species in the catalysts was reduced in the high temperature. With the increase of calcination temperature, the second reduction peak of Ni/MgO was shifted to low temperature, while the first reduction peak area increased. When the catalyst was calcined at 500°C, the two reduction peaks were located at 300°C and 644°C, respectively.

Figure 2 presented H_2 -TPR profiles of the samples Ni/MgO and Ni-Cu/MgO calcined at 500°C. Compared with Ni/MgO, the interaction was weaker between Ni-Cu/MgO and nickel species. As seen from Figure 2, Cu was added to promote the reduction of the nickel species, proved by a significant increase in low-temperature reduction peak area of H_2 -TPR profile of Ni-Cu/MgO. The reduction peaks of Ni-Cu/MgO were located at 290°C, 438°C, and 640°C, respectively. The decrease of the reduction peaks temperatures can

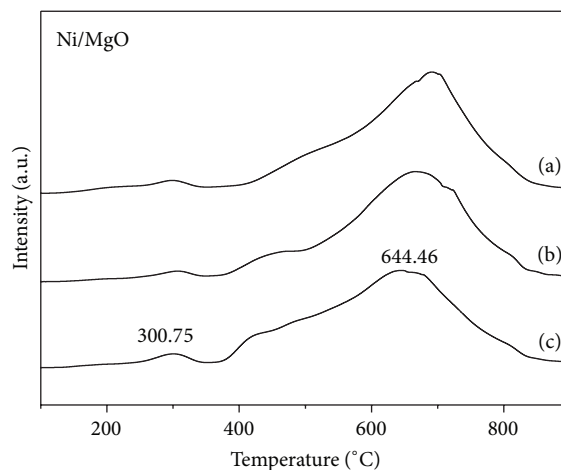


FIGURE 1: H_2 -TPR profiles of Ni/MgO catalysts with various calcination temperatures. (a) 400°C; (b) 450°C; and (c) 500°C.

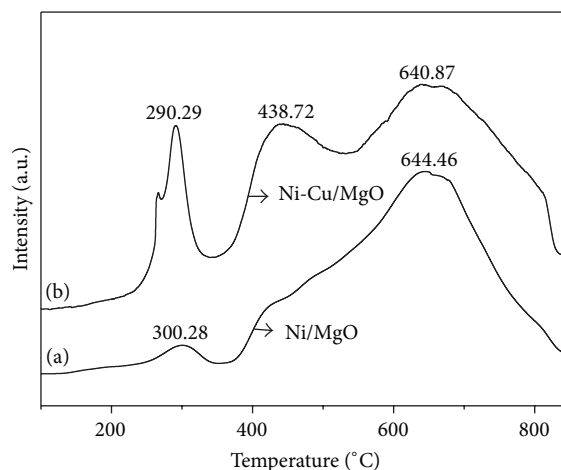


FIGURE 2: H_2 -TPR profiles of the catalysts (a) Ni/MgO and (b) Ni-Cu/MgO calcined at 500°C.

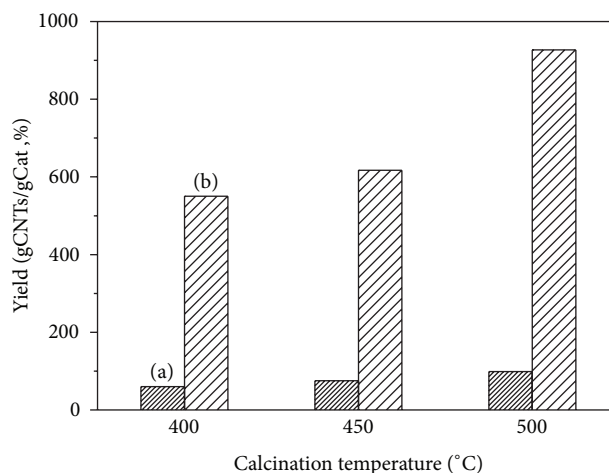


FIGURE 3: Yield of carbon on the catalysts (a) Ni/MgO and (b) Ni-Cu/MgO calcined at different temperatures (reaction temperature at 650°C).

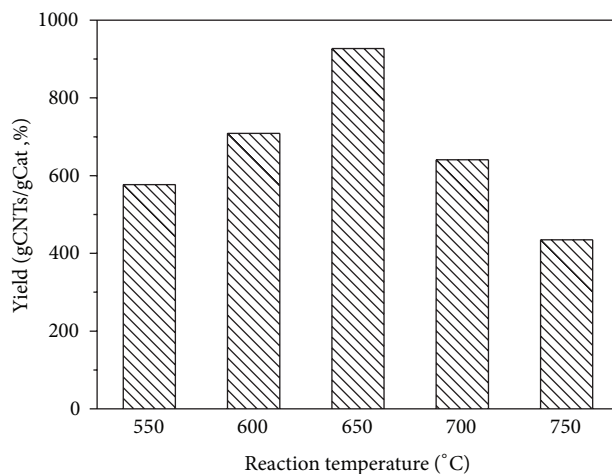


FIGURE 4: Yield of carbon on the catalyst Ni-Cu/MgO calcined at 500°C with different reaction temperatures.

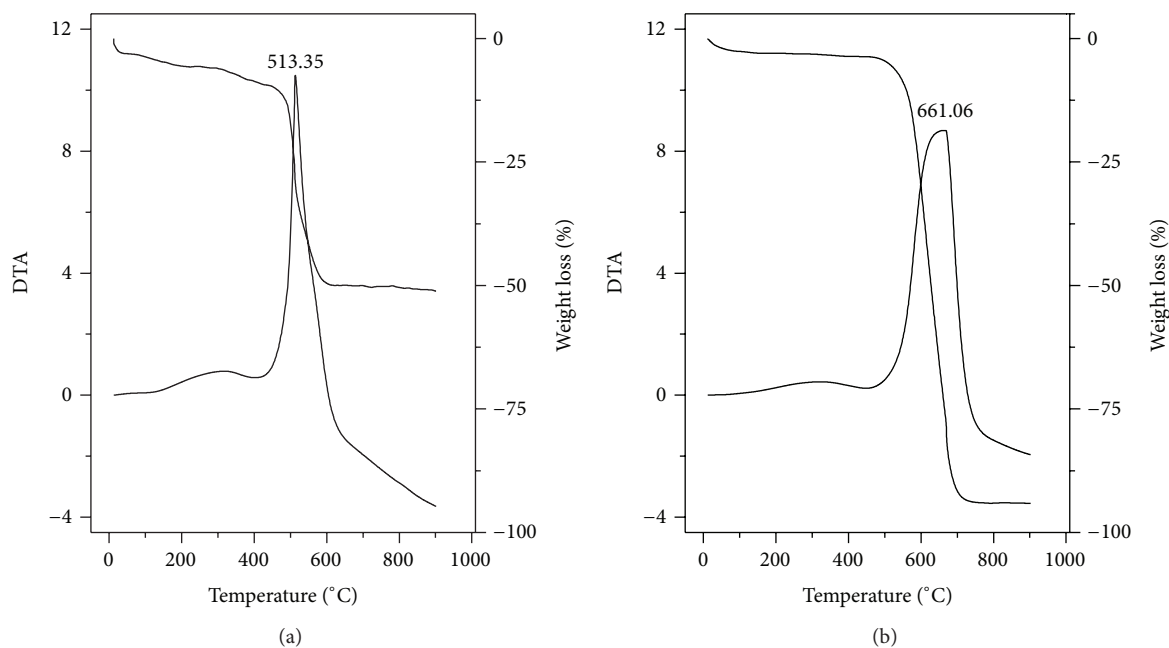


FIGURE 5: TG and DTA curves of the obtained products from the catalysts (a) Ni/MgO and (b) Ni-Cu/MgO calcined at 500°C with reaction temperature 650°C.

be attributed to the overflow effect of hydrogen caused by Cu, which activated hydrogen molecules, thereby promoting the reduction reaction of hydrogen and nickel species at low temperatures.

Figure 3 showed the yield of carbon materials on the catalysts calcined at different temperatures. Compared to the catalyst Ni/MgO, Ni-Cu/MgO had the obvious advantage in the reaction of methane decomposition. It could be noted that the Ni/MgO exhibited very poor activity in the decomposition of methane and growth of carbon materials. Ni/MgO possessed the highest yield of 99%, while the highest yield for Ni-Cu/MgO was 927%. The Cu addition into Ni/MgO significantly increased the catalytic activity of the catalyst and

improved the growth of carbon nanomaterials, which could provide adequate catalytic sites as represented in the H_2 -TPR results shown in Figure 2.

As shown in Figure 4, when the reaction temperature was low, the rate of methane decomposition was limited, thus obtaining few carbon atoms and low CNTs yield. As the reaction temperature increased, the decomposition rate of methane accelerated, and a number of carbon atoms were deposited on the catalyst surface, finally generating CNTs with the high yield. However, when the temperature was too high, the catalyst particles sintered and became large, and then a large amount of carbon deposited on the surface of the catalyst particles, thus lowering the catalyst activity.

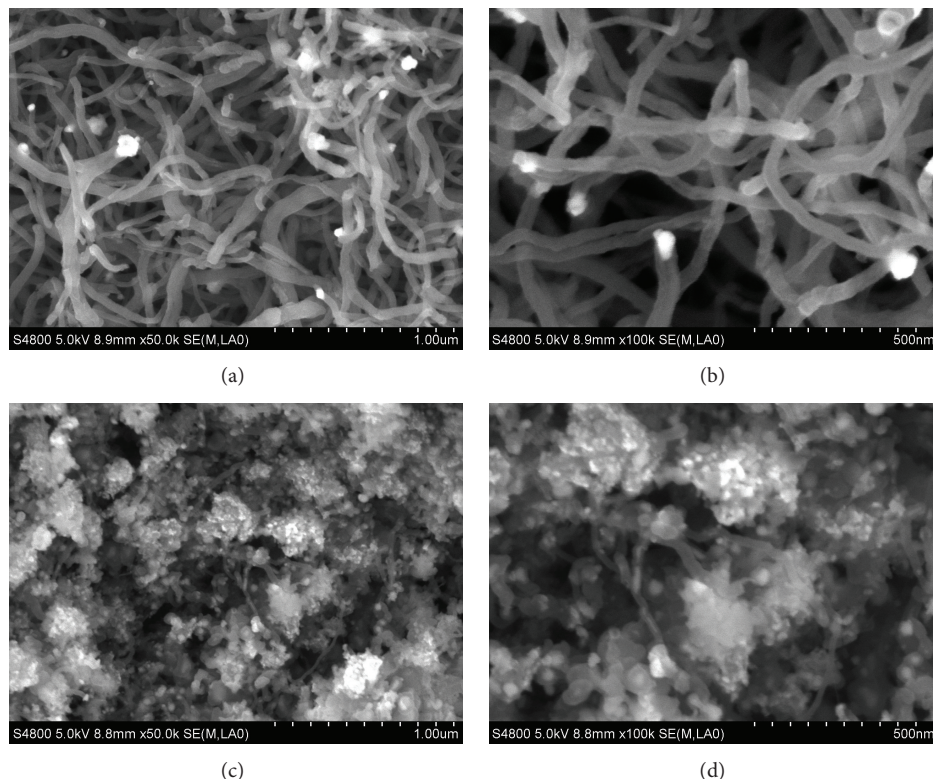


FIGURE 6: SEM images of as-produced materials grown on the catalysts (a), (b) Ni-Cu/MgO and (c), (d) Ni/MgO calcined at 500°C with reaction temperature of 650°C.

Therefore, in order to obtain the high yield of CNTs, the reaction temperature should be appropriate.

Thermogravimetric analysis (TGA) has been widely used for the reaction selectivity of the catalyst and the crystallinity of the as-produced CNTs. Typically, those losses were attributed to the removal of amorphous carbon (300~400°C), CNTs (400~700°C), and massive graphite carbon (>700°C). Figure 5 showed the weight loss of the products during heating in air. Compared with Ni/MgO, the CNTs prepared by Ni-Cu/MgO possessed most of the weight loss (94%) at 400~700°C, indicating high purity of the CNTs. However, less weight loss was associated with CNTs for the products grown on Ni/MgO, only about 51%. It was found that the Ni-Cu/MgO catalyst possessed the highest selectivity toward the growth of CNTs, consistent with the results of SEM images shown in Figure 6.

4. Conclusions

The synthesis of CNTs using Ni/MgO and Ni-Cu/MgO catalysts was studied, and the effect of Cu addition on the carbon yield and structure were investigated. The addition of Cu significantly increased the yield of CNTs. TPR results showed that the Cu addition was effective to improve the reduction of the active nickel component and the catalytic performance of the catalyst. The obtained CNTs on Ni-Cu/MgO catalyst calcined at 500°C with reaction temperature of 650°C were of the greatest yield and quantity.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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