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A Study on Production of Carbon Nanotubes by CH_4 Decomposition over $LaNiO_3$, $La_4Ni_3O_{10}$, $La_3Ni_2O_7$ and La_2NiO_4

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Abstract: Carbon nanotubes (CNTs) of narrow size distribution can be abundantly produced in the catalytic decomposition of CH_4 over pre-reduced $LaNiO_3$, $La_4Ni_3O_{10}$, $La_3Ni_2O_7$ and La_2NiO_4. The CNTs obtained were characterized by means of transmission electron microscopy (TEM). Thermal oxidation of CNTs in air was monitored thermogravimetrically (TG). The results revealed that a lower La/Ni ratio of the catalysts would lead to a wider diameter distribution and a higher degree of graphitic nature.

Keywords: Carbon nanotubes, $LaNiO_3$, La_2NiO_4, $La_3Ni_2O_7$, $La_4Ni_3O_{10}$, CH_4.

Introduction

In the present study, by employing the citric acid complex method[1], we prepared a series of perovskite-type oxides, *viz*. $LaNiO_3$, $La_4Ni_3O_{10}$, $La_3Ni_2O_7$ and La_2NiO_4 for the growth of CNTs. After H_2 reduction, the catalysts turn into La_2O_3 and active component Ni^0 of various sizes. By means of CH_4 decomposition over the reduced catalysts, high quality CNTs with dissimilar diameters can be generated in mass amount. In this paper, we attempt to make a comparison on the structure, graphitic nature among the four kinds of CNTs synthesized over the pre-reduced $LaNiO_3$, $La_4Ni_3O_{10}$, $La_3Ni_2O_7$ and La_2NiO_4 materials, respectively.

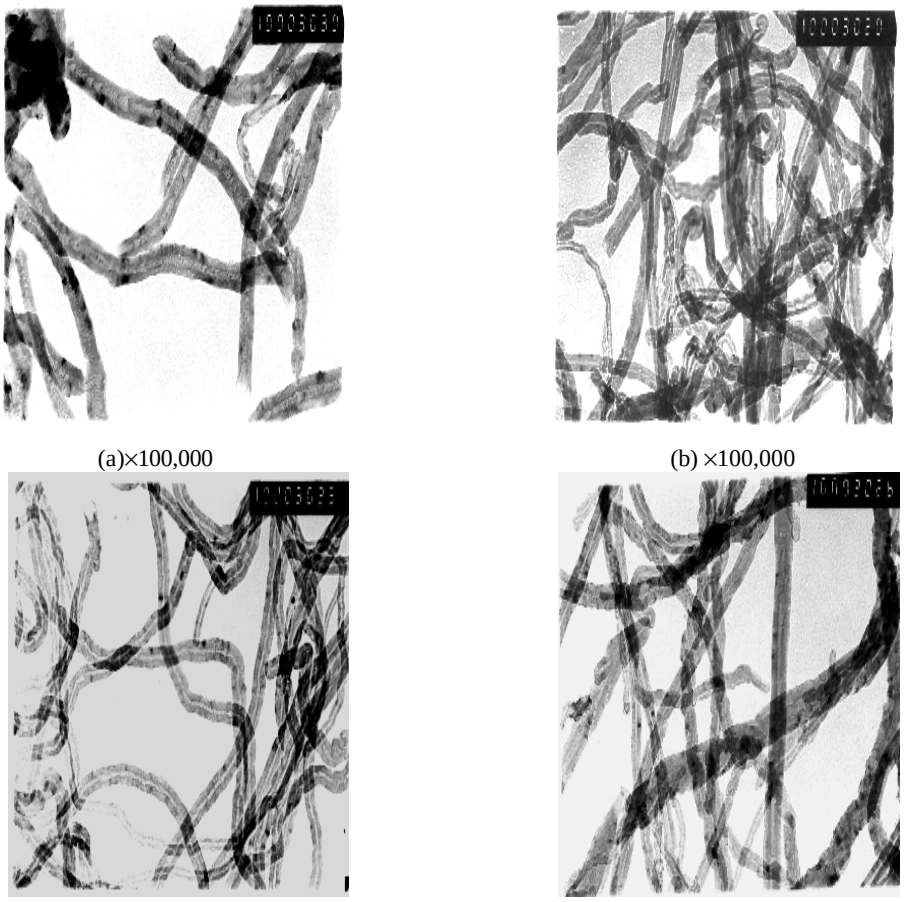
Experimental

The $LaNiO_3$, $La_4Ni_3O_{10}$, $La_3Ni_2O_7$ and La_2NiO_4 catalysts were prepared by complex method. The CNTs were generated by catalytic decomposition of CH_4 over $LaNiO_3$, $La_4Ni_3O_{10}$, $La_3Ni_2O_7$ and La_2NiO_4 in a fluidized-bed catalytic reactor at 750° C for 60 min. The raw CNTs were then treated in nitric acid for purification. The CNTs obtained were characterized by transmission electron microscopy (TEM) (JEOL IEM-100CX). The TGA study of the oxidation of CNTs was performed in air (Perkin-Elmer TGA7).

Results and discussion

Figure 1 shows the typical TEM images of as-synthesized CNTs obtained over different catalysts of nickel composite oxides. One can observe that there are clear differences between the four kinds of CNTs. The range of diameter and the average diameters of

Figure 1 TEM images of CNTs produced over (a) $LaNiO_3$, (b) $La_4Ni_3O_{10}$, (c) $La_3Ni_2O_7$ and (d) La_2NiO_4



(a)×100,000 (b) ×100,000

(c) ×100,000 (d) ×100,000

the CNTs are listed in **Table 1**. With the increase in La/Ni ratio of the catalysts, the CNTs outer- and inner-diameters become smaller.

With the variation of the La/Ni ratio in $La_xNi_yO_z$, the amount of La_2O_3 generated after reduction varied, so the effect of La_2O_3 in preventing Ni^0 from agglomerating varied. According to the XRD results of $La_xNi_yO_z$ reduction in H_2 at 750°C, the estimated size of the Ni^0 particles shows a declining order of $LaNiO_3$>$La_4Ni_3O_{10}$>$La_3Ni_2O_7$>La_2NiO_4. The diameters of CNTs synthesized over $LaNiO_3$, $La_4Ni_3O_{10}$, $La_3Ni_2O_7$, La_2NiO_4 decline in the same order. The present method appears to be promising in the synthesis of

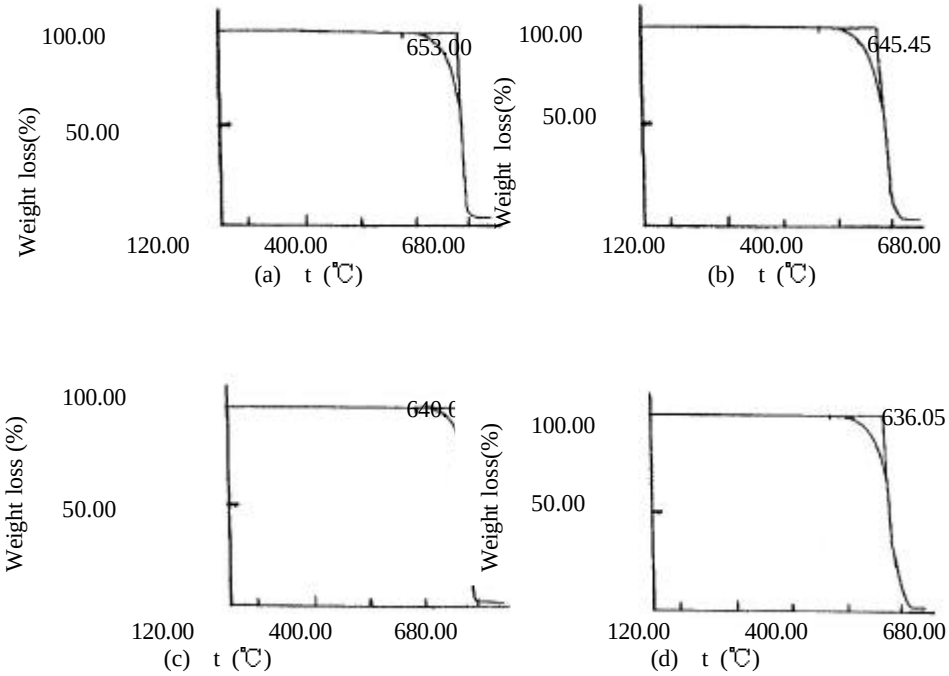
carbon nanotubes in a diameter-controlled manner.

Table 1 The range and average diameter of the CNTs synthesized over the catalysts

	Diameter range (nm)		Average Diameter (nm)	
Catalyst	outer-	inner-	outer-	inner-
$LaNiO_3$	20~45	10~20	35	12
$La_4Ni_3O_{10}$	20~40	6~10	30	10
$La_3Ni_2O_7$	10~30	5~15	25	8
La_2NiO_4	10~40	5~15	20	6

The oxidation of the obtained CNTs has been studied in air by means of thermogravimetry (**Figure 2**). It is clear that the threshold temperatures for the oxidation of the CNTs obtained over the $LaNiO_3$, $La_4Ni_3O_{10}$, $La_3Ni_2O_7$ and La_2NiO_4 samples were *ca* 653.00°C, 645.45°C, 640.09°C and 636.05°C, respectively, about 220°C higher than that reported by Kukovitskii (*ca* 420°C)[2]. It has been reported that graphite could be oxidized in air at *ca* 520°C[2]. For the CNTs, which are more graphitic in nature, threshold temperature for oxidation should be higher.

Figure 2 The TG plot during oxidation of CNTs prepared over (a) $LaNiO_3$, (b) $La_4Ni_3O_{10}$, (c) $La_3Ni_2O_7$ and (d) La_2NiO_4



Probably, the increase of La content in the catalysts influences the degree of graphitic nature and quality of the CNTs produced. We observed that the lower the La/Ni ratio is,

the higher is the graphitic nature and thermal resistance in air.

Conclusion

The reduced $LaNiO_3$, $La_4Ni_3O_{10}$, $La_3Ni_2O_7$ and La_2NiO_4 are good catalysts for the mass production of CNTs with enhanced graphitic nature. The diameter of the CNTs can be confined to a narrow range through the variation of the La/Ni ratio.

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