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Synthesis of single-walled carbon nanotubes using binary (Fe, Co, Ni) alloy nanoparticles prepared in situ by the reduction of oxide solid solutions

E. Flahaut ^a, A. Govindaraj ^{b,c}, A. Peigney ^a, Ch. Laurent ^a, A. Rousset ^a,
C.N.R. Rao ^{b,c,*}

^a *Laboratoire de Chimie des Matériaux Inorganiques, ESA CNRS 5070, Université Paul-Sabatier, F-31062 Toulouse Cedex 4, France*

^b *CSIR Centre of Excellence in Chemistry, Indian Institute of Science, Bangalore 560012, India*

^c *Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P.O., Bangalore 560064, India*

Abstract

Passing a H₂-CH₄ mixture over oxide spinels containing two transition elements as in Mg_{0.8}M_yM'_zAl₂O₄ (M, M' = Fe, Co or Ni, y + z = 0.2) at 1070°C produces small alloy nanoparticles which enable the formation of carbon nanotubes. Surface area measurements are found to be useful for assessing the yield and quality of the nanotubes. Good-quality single-walled nanotubes (SWNTs) have been obtained in high yields with the FeCo alloy nanoparticles, as evidenced by transmission electron microscope images and surface area measurements. The diameter of the SWNTs is in the 0.8–5 nm range, and the multiwalled nanotubes, found occasionally, possess very few graphite layers. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Carbon nanotubes are attracting much attention because of their novel mechanical and electronic properties. In order to suitably make use of the nanotubes, it is necessary to have them in uniform size, with a narrow size distribution. Towards this purpose, most workers employ metal particles to catalyse the decomposition of hydrocarbons or carbon monoxide. The metal particles are suggested to play a catalytic role at an atomic level rather than as heterogeneous nucleation sites [1]. Although Ni and

Co nanoparticles appear to be the best amongst monometallic catalysts, nanoparticles of bimetallic alloys formed by these metals give 10–100 times higher yields of single-walled nanotubes (SWNTs) [2,3]. If the particle size of the metals and alloys is large, carbon filaments or fibres rather than the Iijima-type nanotubes are generally obtained [4–8]. Small nanoparticles of transition metals produced by the pyrolysis of organometallics containing Fe, Co and Ni along with hydrocarbons give multiwalled nanotubes (MWNTs), but through a careful manipulation of partial pressures, SWNTs are obtained [9,10]. We have employed reduced spinel oxides containing small quantities of two transition metals (amongst Fe, Co, and Ni) to synthesize nanotubes,

* Corresponding author. E-mail: cnrrao@sscu.iisc.ernet.in

since the method is known to give rise to narrow compositions of small alloy nanoparticles [11].

In the method employed in the present study, high-temperature hydrogen reduction of the oxide spinels of the general composition $Mg_{0.8}M_yM'_zAl_2O_4$ ($M, M' = Fe, Co, Ni, y + z = 0.2$ and y or $z = 0.05, 0.10, 0.15$ and 0.20) generates catalytic transition metal alloy nanoparticles required for the formation of the nanotubes by the pyrolysis of methane. Surface area measurements have been employed to quantify the yield and quality of nanotubes. High-quality SWNTs have been obtained particularly with FeCo alloy nanoparticles.

2. Experimental

Spinel oxides of the general formula $Mg_{0.8}M_yM'_zAl_2O_4$ ($M, M' = Fe, Co, Ni, y + z = 0.2$ and y or $z = 0.05, 0.10$ and 0.15) were prepared starting with a stoichiometric mixture of the metal nitrates and subjecting the nitrate mixture along with urea to the usual procedure employed in combustion synthesis [12]. The combustion product was attrition-milled in a Nylon vessel in an aqueous medium, passed through a sieve, washed with ethanol

Table 1
Some characteristics of the carbon nanotubes obtained in the present study

Specimen ^a	C_n (wt%)	S_r ($m^2 g^{-1}$)	S_o ($m^2 g^{-1}$)	ΔS ($m^2 g^{-1}$)	$\Delta S/C_n$ ($m^2 g^{-1}$)
Fe	5.81	18.20	10.48	7.72	133
Fe _{0.75} Co _{0.25}	7.10	25.06	10.14	14.92	210
Fe _{0.50} Co _{0.50}	6.99	31.65	11.79	19.86	284
Fe _{0.25} Co _{0.75}	5.61	25.29	10.41	14.88	265
Co	3.77	23.27	10.52	12.75	338
Fe	5.81	18.20	10.48	7.72	133
Fe _{0.75} Ni _{0.25}	5.12	20.01	10.05	9.96	195
Fe _{0.50} Ni _{0.50}	4.07	19.55	10.15	9.40	231
Fe _{0.25} Ni _{0.75}	2.58	15.17	8.75	6.42	249
Ni	1.97	13.54	9.20	4.34	220
Co	3.77	23.27	10.52	12.75	338
Co _{0.75} Ni _{0.25}	2.39	19.14	11.29	7.85	328
Co _{0.50} Ni _{0.50}	1.75	13.22	8.70	4.52	259
Co _{0.25} Ni _{0.75}	2.00	15.67	8.93	6.74	338
Ni	1.97	13.54	9.20	4.34	220

^aMetal content was 6.7 wt% in all the compositions.

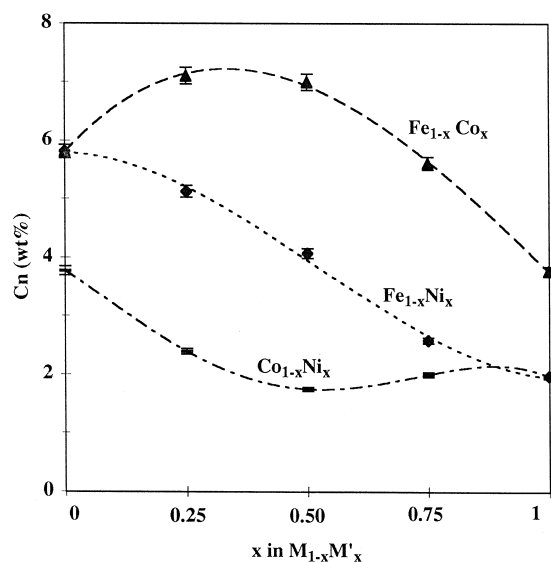


Fig. 1. Variation of the carbon content (C_n) with the composition of the alloy nanoparticle. The dashed lines are guides to the eye.

and calcined at 500°C for 30 min. The oxide product contained essentially the lacunar spinel phase [11,13] of the general formula $D_{1-3\alpha}T_{2+2\alpha}(\)_{\alpha}O_4$, where D and T stand for divalent and trivalent cations and () represents vacancies. A dry mixture of H_2-CH_4 (18 mole% CH_4) was passed over the calcined oxide at 1070°C for 6 min at a flow rate of 250 sccm. This resulted in the reduction of the transition metal ions to the metals in the form of nanoparticles, followed by the formation of carbon nanotubes, the entire process was very facile. We shall designate the various samples by $M_{1-x}M'_x$ ($M, M' = Fe, Co, Ni$) for brevity.

The carbon content, C_n , of the products subjected to the H_2-CH_4 treatment, containing carbon (in the form of nanotubes) along with the metal particles and the oxide, was determined by flash combustion. The values of C_n so obtained are listed in Table 1. The products after H_2-CH_4 treatment were oxidized in air at 900°C for 2 h to eliminate the carbon. The composition of the transition metal alloy clearly affects the conversion of CH_4 to carbon by hydrogen reduction. The values of C_n are plotted against the alloy composition in Fig. 1. Fe_{0.75}Co_{0.25} and Fe_{0.50}Co_{0.50} appear to be most efficient in terms of the carbon yield.

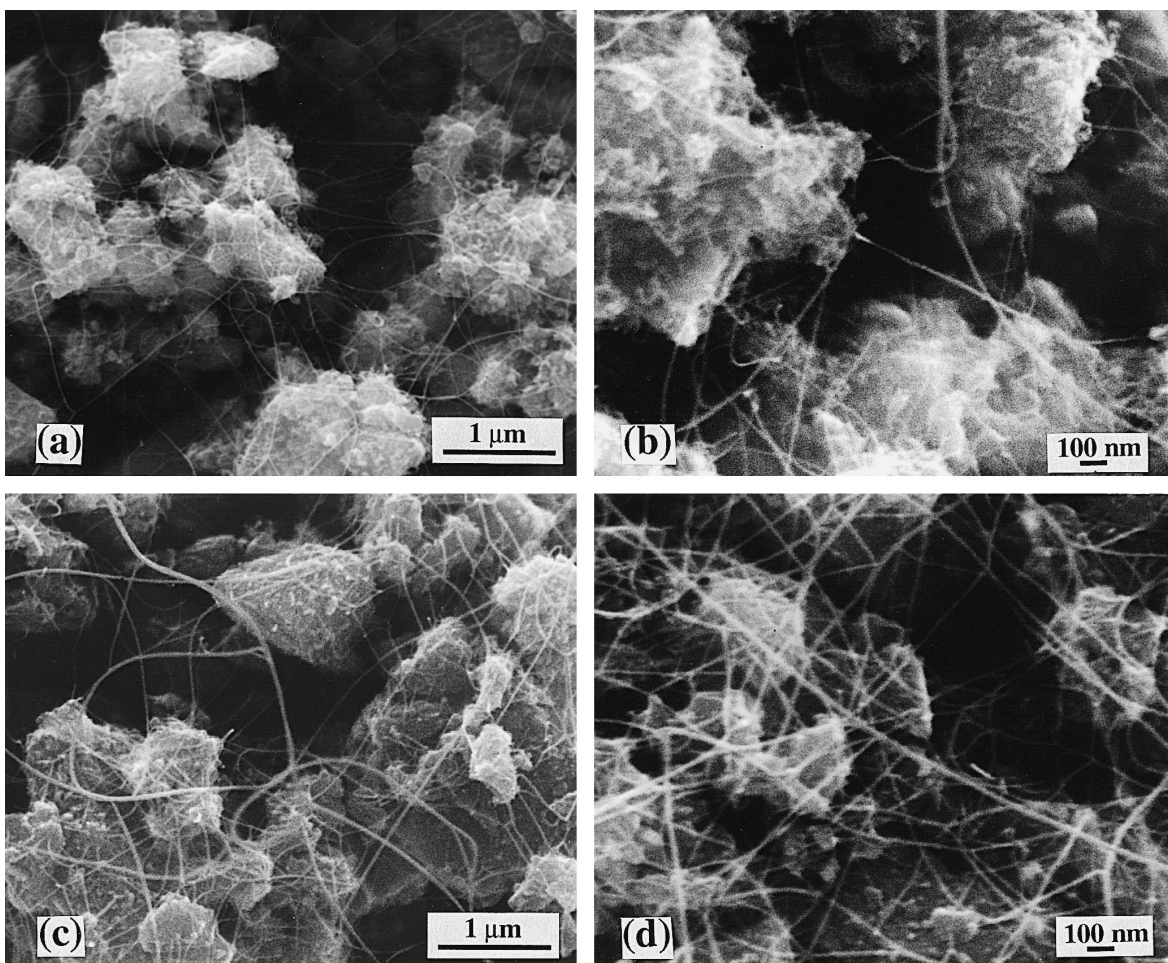


Fig. 2. SEM images of the product obtained by treatment of oxide spinels with the $\text{CH}_4\text{-H}_2$ mixture: (a) and (b) $\text{Fe}_{0.5}\text{Co}_{0.5}$; (c) and (d) $\text{Fe}_{0.5}\text{Ni}_{0.5}$.

BET¹ surface areas of the following materials were measured by N_2 adsorption: reduced product after passing the $\text{H}_2\text{-CH}_4$ mixture and hence containing carbon along with metal particles (S_r) and the material obtained after oxidizing the product of $\text{H}_2\text{-CH}_4$ treatment and hence free of carbon (S_o). The values of the surface areas are listed in Table 1. The products obtained after passing the $\text{H}_2\text{-CH}_4$ mixture over the oxide spinels were examined by X-ray diffraction (XRD), scanning electron microscopy (SEM) as well as transmission electron microscopy (TEM).

¹ Brünauer–Emmett–Teller adsorption isotherm.

3. Results and discussion

The XRD patterns of the products obtained after subjecting the oxide spinels containing the transition metals to treatment with the $\text{H}_2\text{-CH}_4$ mixture at 1070°C showed evidence for the presence of metal or alloy particles (depending on the starting composition) and the oxide spinel, $\text{Mg}_{0.8}\text{Al}_{2.133}(\text{O})_{0.067}\text{O}_4$ where (O) represents a vacancy. Thus, the oxide composition containing only Co gave reflections due to $\epsilon\text{-Co}$ whereas those with both Co and Ni gave reflections due to the alloys of the respective compositions. Reflections due to Fe–Ni and Fe–Co alloys were similarly found in the corresponding oxide compositions. With the iron-containing oxide spinel,

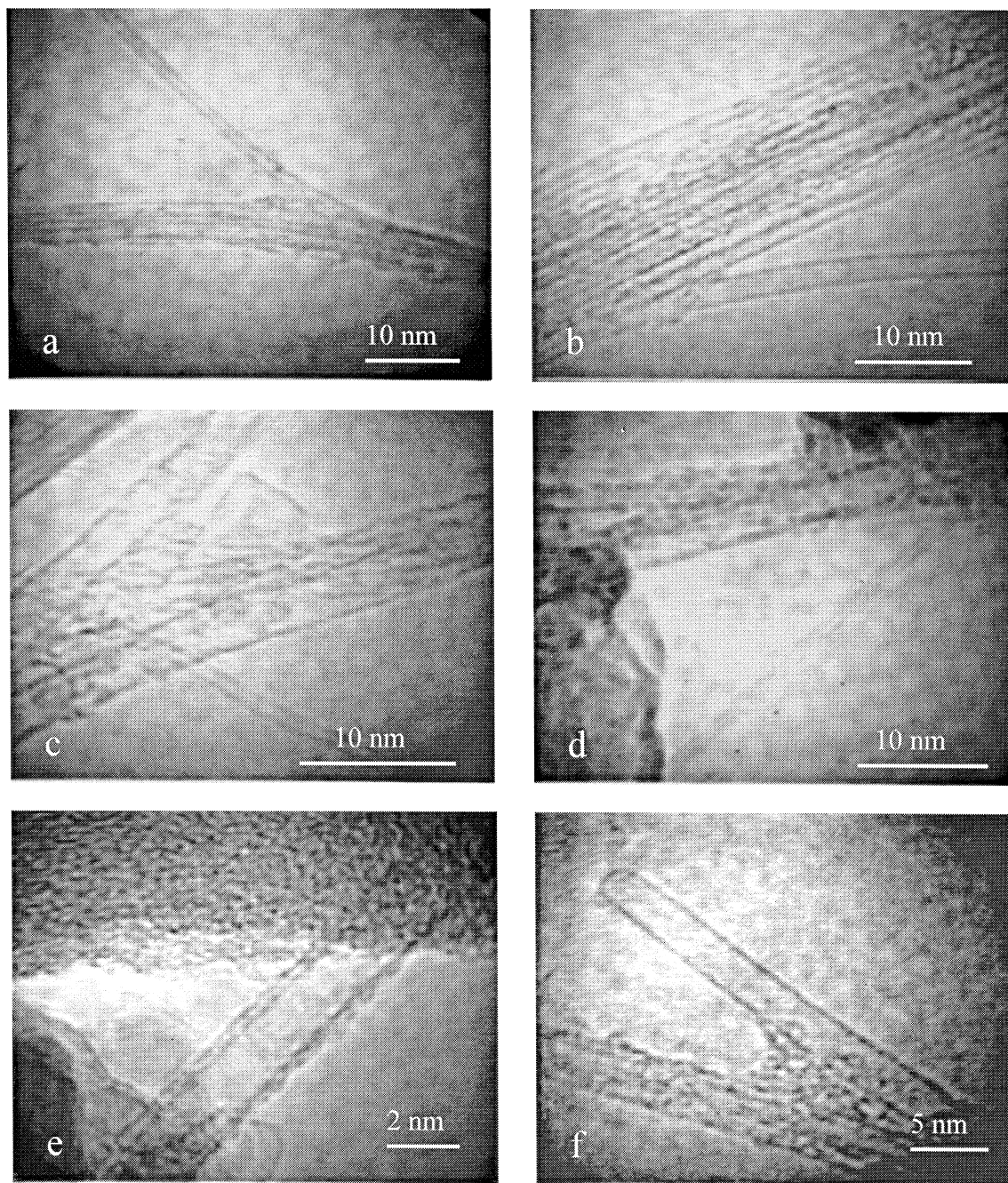


Fig. 3. TEM images of the nanotubes obtained with $\text{Fe}_{0.50}\text{Co}_{0.50}$ nanoparticles: (a) a single-wall nanotube (noted SWNT hereafter) 1.1 nm in diameter emerges from a bundle the diameter of which is ~ 4 nm; (b) the largest observed bundle, ~ 14 nm in diameter, with an emerging SWNT, 2 nm in diameter; (c) the thinnest observed SWNT, 0.8 nm in diameter, superimposed with two larger SWNTs; (d) a tight SWNT, 0.85 nm in diameter, with neighbouring larger tubes (between 1.6 and 2.8 nm in diameter); (e) a nanotube with 2 walls (2.1 nm in diameter); (f) a SWNT, 2.5 nm in diameter, with a closed hemisphere tip.

reflections due to Fe_3C were found as well as those due to $\alpha\text{-Fe}$. Clearly, treatment with the $\text{H}_2\text{-CH}_4$ mixture not only reduces the transition metal ions into the metallic state, but also forms binary alloys when two metal ions are present.

The SEM images of the oxide spinels subjected to the $\text{H}_2\text{-CH}_4$ treatment showed the presence of nanotubes in the form of a web-like network of long filaments. In Fig. 2, we show typical SEM images. The images generally reveal the presence of bundles of nanotubes, the bundle diameters varying with the composition of the alloy particles. Thus, with $\text{Fe}_{0.50}\text{Ni}_{0.50}$ and $\text{Co}_{0.50}\text{Ni}_{0.50}$, the bundle diameters are in the 20–50 and 10–20 nm ranges, respectively. Individual filaments are generally much smaller than 5 nm in diameter. The SEM image with $\text{Fe}_{0.50}\text{Co}_{0.50}$ particles shows very few nanotubes mainly because the nanotubes and their bundles are considerably smaller than 10 nm in diameter. The presence of large quantities of single-walled nanotubes in the case of $\text{Fe}_{0.50}\text{Co}_{0.50}$ could, however, be definitively established from the TEM images. SEM fails to reveal such thin nanotubes because of the limitation of the resolution. In Fig. 3, we show typical TEM images revealing the presence of isolated SWNTs as well as bundles of SWNTs. Fig. 3a shows a SWNT 1.1 nm in diameter emerging from a bundle of 4 nm diameter. Amorphous carbon deposits present on the bundle result from the degradation of the nanotubes under electron beam irradiation. Pristine samples accordingly show little of such deposits. The largest bundle observed by us is ~ 14 nm in diameter (Fig. 3b). An emerging SWNT, 2 nm in diameter, can be seen at the bottom of this image. In Fig. 3c, we show the thinnest SWNT (0.8 nm in diameter) observed by us; it is superimposed by two larger SWNTs, the walls of which are irregular because of degradation under the electron beam. A straight SWNT (0.85 nm in diameter) along with larger ones (between 1.6 and 2.8 nm in diameter) are shown in Fig. 3d. A nanotube (2.1 nm in diameter) with two walls is seen in Fig. 3e. It is interesting that most of the isolated nanotubes ($\sim 80\%$) are SWNTs with diameters in the 0.8–5 nm range. Multiwalled nanotubes found occasionally have diameters smaller than 10 nm, and generally possess only two graphite layers. Those with 3, 4 and 5 graphitic sheaths were rarely observed. In Fig. 3f, a SWNT (2.5 nm in diameter)

with a closed hemispheric tip is seen coming out of a thin bundle (3 nm in diameter). Interestingly, no catalyst particle is present at the tube tip.

From the values of the surface areas before and after $\text{H}_2\text{-CH}_4$ treatment (Table 1), we can obtain the contribution to the surface area by the carbon formed by the decomposition of CH_4 [14]. We list the $\Delta S = S_t - S_0$ values in Table 1. We show the variation of ΔS with the composition of the alloy nanoparticles in Fig. 4. The alloys are generally associated with higher ΔS values than either component metal, and the highest values are found with the Fe–Co alloys. The $\Delta S/C_n$ values, corresponding to the surface area per gram of carbon (produced by the decomposition of CH_4) may be taken to represent the quality of the nanotubes, a higher figure denoting a smaller tube diameter as well as a greater nanotube yield. We have listed the $\Delta S/C_n$ values in Table 1 and plotted them against the composition of the metal alloy particles in Fig. 5. A progressive increase in $\Delta S/C_n$ is observed with the Co content in the Fe–Co system, the Fe–Ni system shows such an increase with the Ni content partially. In the case of the Co–Ni system, $\Delta S/C_n$ actually decreases with the Ni content. The $\Delta S/C_n$ values in the alloys are generally in the range $195\text{--}338\text{ m}^2\text{ g}^{-1}$, the highest

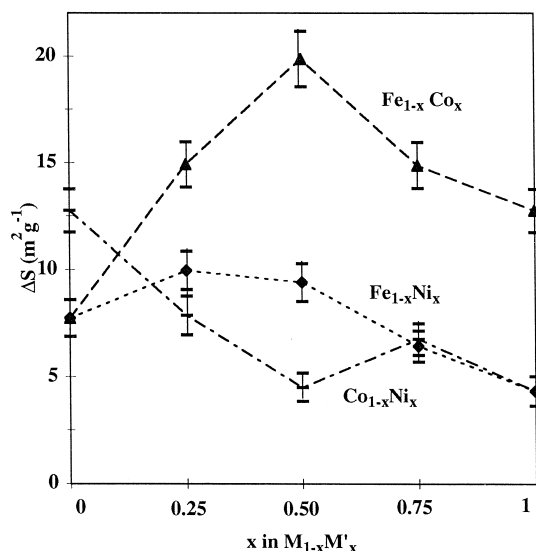


Fig. 4. Variation of the surface area due to the carbon product, ΔS , with the composition of the alloy nanoparticles. The dashed lines are guides to the eye.

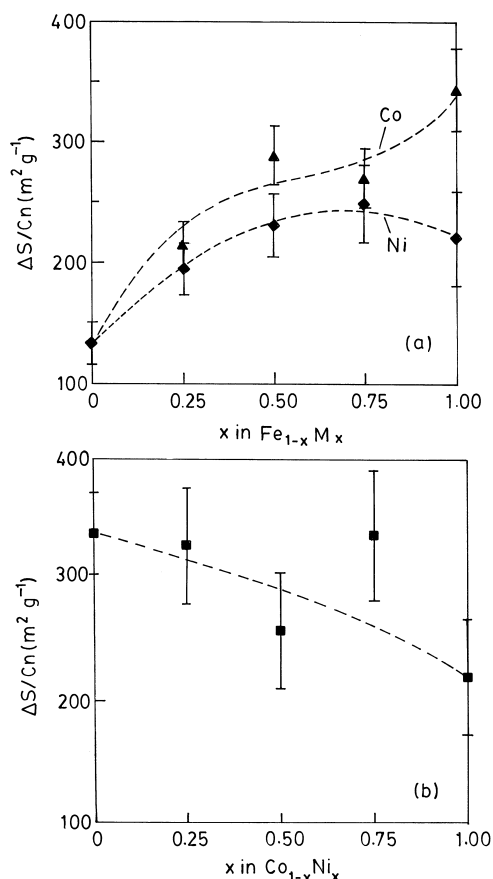


Fig. 5. Surface area per gram of carbon, $\Delta S/C_n$, plotted against the composition of the alloy nanoparticles. The dashed lines are guides to the eye.

value corresponding to that found with cobalt alone. The $\Delta S/C_n$ values found by us indicate that both Fe–Co and Co–Ni alloy particles yield high-quality nanotubes, the presence of Co is probably responsible for the effect. Interestingly, TEM studies also show that the $\text{Fe}_{0.5}\text{Co}_{0.5}$ alloy gives the highest yield of SWNTs as discussed earlier. The $\Delta S/C_n$ values found by us are close to the recently reported surface area of $268 \text{ m}^2 \text{ g}^{-1}$ for multi-walled nanotubes [15].

The above results show that transition metal alloy nanoparticles produced by the reduction of oxide spinels are good agents for generating single-walled nanotubes. This is consistent with the earlier observation [11] that reduction of spinels gives relatively small nanoparticles with a narrow size distribution. It

is indeed known that the small size of the nanoparticles is essential to form SWNTs [10,16]. The presence of a metal such as Co appears to prevent the formation of Fe_3C and such carbides. It is likely that the oxide support affords a good distribution of the alloy nanoparticles on its surface. Alloying promotes the decomposition of CH_4 to produce carbon nanotubes, the quality of which depends on the alloy composition. It is noteworthy that the best performance is found with FeCo nanoparticles which give a high yield of SWNTs of good quality, as judged both by electron microscopy and surface area measurements. The successful synthesis of good-quality SWNTs reported here by using FeCo alloy nanoparticles dispersed on oxide spinels is to be compared with the recent report of Kong et al. [17] who obtained SWNTs by chemical vapor deposition of CH_4 over impregnated $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ at low loading. These workers could not quantify the yield or quality of the nanotubes.

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