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Alumina and silica supported metal catalysts for the production of carbon nanotubes

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Abstract

Catalytic activity of iron, cobalt and a mixture of iron and cobalt supported on Al_2O_3 and SiO_2 has been investigated in the production of carbon nanotubes (NTs). The supports are obtained from different methods. Acetylene was used as the source of carbon and nitrogen as the carrier gas. The pyrolysis of hydrocarbon was carried out at 500, 600 and 700 °C. The effect of other reaction parameters such as rate of flow of the hydrocarbon, carrier gas and the reaction time has also been investigated. Transmission electron microscope (TEM) was used to follow the quality and nature of NTs formed. It was observed that a good quality and quantity of multiwall carbon nanotubes (MWNTs) were produced when alumina prepared from aluminum isopropoxide and deposited with a mixture of iron and cobalt catalysts was used.

Keywords: Carbon nanotubes; Alumina; Silica; Acetylene; Catalytic method

1. Introduction

Tubular derivatives of fullerenes, popularly known as carbon nanotubes (NTs), were first observed in arc discharge method [1]. NTs exhibit properties, which are different from those of the closed cage fullerenes such as C60, C70, C76, etc. The unique and interesting properties of carbon tubes directly result from their special topologies. In the last 10 years, the importance of NTs has grown by leaps and bounds. Their importance as novel carbon materials has earned them a place of pride in the field of material science research. Several review articles dealing with the various aspects of NTs have been published [2–11]. Due to their high mechanical strength, capillary properties and remarkable electronic structures, a wide range of potential uses has been envisaged [12–15]. NTs have also been used as supports for metals in the field of heterogeneous catalysis [16], material for hydrogen storage [17], as composite materials in polymer science [18,19] and for immobilization of proteins and enzymes [20]. Several techniques like arc discharge, laser ablation and catalytic methods and others are developed for the production of NTs [21]. Recently many material science chemists and physicists have turned their attention onto the development of methods for the production of NTs in large-scale to realize their speculated applications [22,23]. Among these, catalytic methods seems to be one of the most promising methods for large-scale production of carbon tubes. Metal and mixture of metals supported on oxides, clays and

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zeolites have been found to be active as catalysts in the production of NTs [24–27]. Various mechanisms proposed for nanotubes nucleation and growth from nanometric metal particles have been reviewed [28].

In the field of heterogeneous catalysis, a number of oxides and mixed oxides have been used to disperse and stabilize metallic particles [29]. Catalytic properties of these solids are known to depend upon the interaction between the support and the metal particles, which in turn depends on their method of preparation. Therefore, it is interesting to investigate the influence of the support on the catalytic activity of metals in the synthesis of NTs. In the present study, we have attempted to synthesize NTs over Al_2O_3 and SiO_2 supported Fe, Co and Fe–Co catalysts. We will focus on the effect of the method of support preparation on the catalytic activity of the metal particles. In addition, the influence of the reaction temperature and the rates of flow of the hydrocarbon and the carrier gas are also investigated to produce good quality and quantity of carbon tubes.

2. Experimental

2.1. Catalysts preparation

Al_2O_3 and SiO_2 were obtained from different sources. Hydrated alumina prepared from aluminum isopropoxide in the laboratory is designated as Al_2O_3(P) and that of a commercial sample (corundum alumina) used as Al_2O_3(C). Silica supports used were either prepared by sol–gel method or obtained from a commercial source (silica-60 Aldrich). These silica supports are represented as SiO_2(SG) and SiO_2(C), respectively. All the supports were impregnated with acetate salt solutions of either Fe or Co or a mixture of Fe and Co so as to get 2.5 wt.% of the metal on the support. Further details of the methods of preparation of all the support–metal mixtures are reported elsewhere [30]. The support–metal mixtures thus prepared will be represented as catalysts in the following text.

2.2. NTs production

The experiments to produce NTs were carried out in a horizontal flow furnace at atmospheric pressure. The catalyst was spread on long quartz boat, which was placed inside a quartz tube. The reaction mixture containing acetylene and nitrogen gas in a definite proportion was passed over the catalyst bed for a pre-determined time. The experiments were carried out at three different temperatures: 500, 600 and 700 °C. The percentage of carbon deposited due to the catalytic decomposition of acetylene was obtained from the following equation:

$$\text{Carbon deposit (\%)} = 100\frac{(m_{\text{tot}} - m_{\text{cat}})}{m_{\text{cat}}},$$

where m_{cat} and m_{tot} are the mass of the catalyst before and after the reaction, respectively.

2.3. Characterization of the carbon deposit

Formation of NTs was followed by TEM. Samples for TEM analysis were prepared as described earlier [30].

3. Results and discussion

It is observed that at 500 °C, none of the catalysts was active in the formation of carbon tubes. Generation of NTs was observed only in the carbon deposit obtained from reactions carried out at 600 and 700 °C.

3.1. Effect of the catalyst and reaction conditions on the carbon deposit

The percentage of carbon deposited on the catalyst due to the catalytic decomposition of acetylene increased when the reaction temperature was raised from 600 to 700 °C. The increase in the carbon deposit with increase in the reaction temperature is more pronounced in the case of alumina containing a mixture of Fe and Co than when it had either Fe or Co as detailed in Table 1.

The effect of other reaction parameters is as follows. At 600 °C and at lower flow rate of acetylene (10 ml/min), the carbon deposit decreased with an increase in the rate of flow of N_2 from 75 to 120 ml/min in the case of all the catalysts used. This may be due to the decrease in the contact time of the hydrocarbon with increase in the flow of the carrier gas. However, at higher flow rates of acetylene gas, a change in the amount of N_2 flow did not show any marked change

Table 1
Carbon deposit (%) from acetylene decomposition on Al_2O_3(P) supported metal(s) at two different reaction temperatures[a]

Metal(s)	Nitrogen flow (ml/min)	Acetylene flow (ml/min)	Carbon deposit (%) depending on the reaction time	
			30 min	60 min
Co	75	10	6.4 (8.6)	20.0 (20.5)
		15	8.3 (9.4)	21.8 (18.3)
	120	10	8.2 (6.2)	21.8 (18.3)
		15	13.2 (8.6)	26.8 (23.5)
Fe	75	10	8.4 (5.6)	21.7 (15.1)
		15	9.7 (6.4)	21.4 (16.9)
	120	10	11.4 (4.8)	30.2 (9.3)
		15	13.1 (7.1)	33.3 (17.6)
Co/Fe	75	10	14.3 (8.6)	28.0 (18.5)
		15	16.4 (15.3)	49.5 (21.7)
	120	10	12.4 (9.6)	32.5 (16.8)
		15	24.0 (15.6)	43.1 (18.7)

[a] Values given in the parentheses refer to the wt.% of carbon deposit obtained at 600 °C and those figures not in the parenthesis refer to the wt.% of carbon deposit obtained at 700 °C.

in the percentage of carbon deposit. When the reaction temperature is raised to 700 °C, the carbon deposit increased with increase in the rate of flow of acetylene as well as of the carrier gas. An increase in both the time and the flow rate of acetylene showed a marked increase in carbon deposit. However, experiments carried out at different flow rates of C_2H_2 and for different reaction times indicate that a flow of acetylene at 15 ml/min for 60 min results in a better conversion of acetylene into NTs.

It is well established and documented [29] that the support plays an important role in determining the catalytic activity of a metal present in it. The state of the metal on a support depends on the kind of metal–support interaction which in turn depends on the nature of the support and preparation method. Realizing the importance of the support in determining the catalytic activity of metal particles deposited on it, an attempt was made to find out the influence of the nature of the support on the catalytic activity of Fe, Co and Fe–Co in the production of nanotubes. According to previous results [31], the diameter of NTs growing on a metal particle mainly depends on the dispersion of the metal particles on the support.

The data presented in Table 2 indicate that the method of preparation of the support plays an important role in determining the dispersion and hence the catalytic activity of the metals in the production of NTs by the catalytic decomposition of C_2H_2. Alumina obtained by the hydrolysis of aluminum isopropoxide seems to the best candidate as a support for Fe and/or Co catalysts, whereas commercial alumina-based catalysts show negligible activity. Hydrolysis of aluminum isopropoxide results in $Al(OH)_3$ gel, which on drying yields hydrated alumina. This is basic due to the presence of surface hydroxyl groups. When this alumina is mixed with salt solutions of Fe/Co, there is a possibility of better mixing and homogeneous distribution of salt than that would be obtained in the case of commercial Al_2O_3 which is neutral. This accounts for higher catalytic activity of Fe, Co and Fe–Co on Al_2O_3(P) than on Al_2O_3(C) because as already mentioned one of the major factors influencing the activity is the nature of distribution of the

Table 2
Carbon deposit (%) from acetylene decomposition at 700 °C on different metal(s) support catalysts (C_2H_2, 15 ml/min; N_2 15 ml/min; 60 min reaction)

Support	Carbon deposit (%) depending on the metal(s)		
	Co	Fe	Fe–Co
Al_2O_3(P)	22.2	21.4	49.5
Al_2O_3(C)	1.5	1.8	3.7
SiO_2(SG)	8.9	8.0	31.7
SiO_2(C)	3.0	5.9	21.3

metal(s) particles on the support. Laurent et al. [32] have synthesized NTs over Fe–Al_2O_3 nanocomposite powders obtained by selective reduction of different $Al_{1.8}Fe_{0.2}O_3$ solid solutions at 900 or 1000 °C and noticed that the activity of the catalysts and the nature of the nanotubes produced were different and depended on the size of the catalyst particle.

Metal(s) when supported on silica obtained by sol–gel method SiO_2(SG) resulted in only a moderate generation of carbon deposit (Table 2). However, it showed higher activity in the formation of NTs than the commercial sample. This is probably due to the fact that sol–gel method results in the distribution of metal ions in a highly homogeneous manner. Lower activity of SiO_2(SG) compared to Al_2O_3 supported metals indicates that the size of the metal particles produced in the former is somewhat larger than the average nanometer scale clusters required for producing NTs. It is appropriate to mention here that we have also investigated the catalytic activity of Co supported on Al_2O_3(P) containing different amounts of SiO_2 and the results were published elsewhere [30]. It was observed that alumina–silica systems containing 20 wt.% of Al showed very high activity towards MWNTs formation.

One important point to be considered while selecting a support for a metal when preparing a catalyst is probably that it should not only result in a high density of NTs, but also be separated easily from the carbon deposit by a suitable and simple method to obtain pure

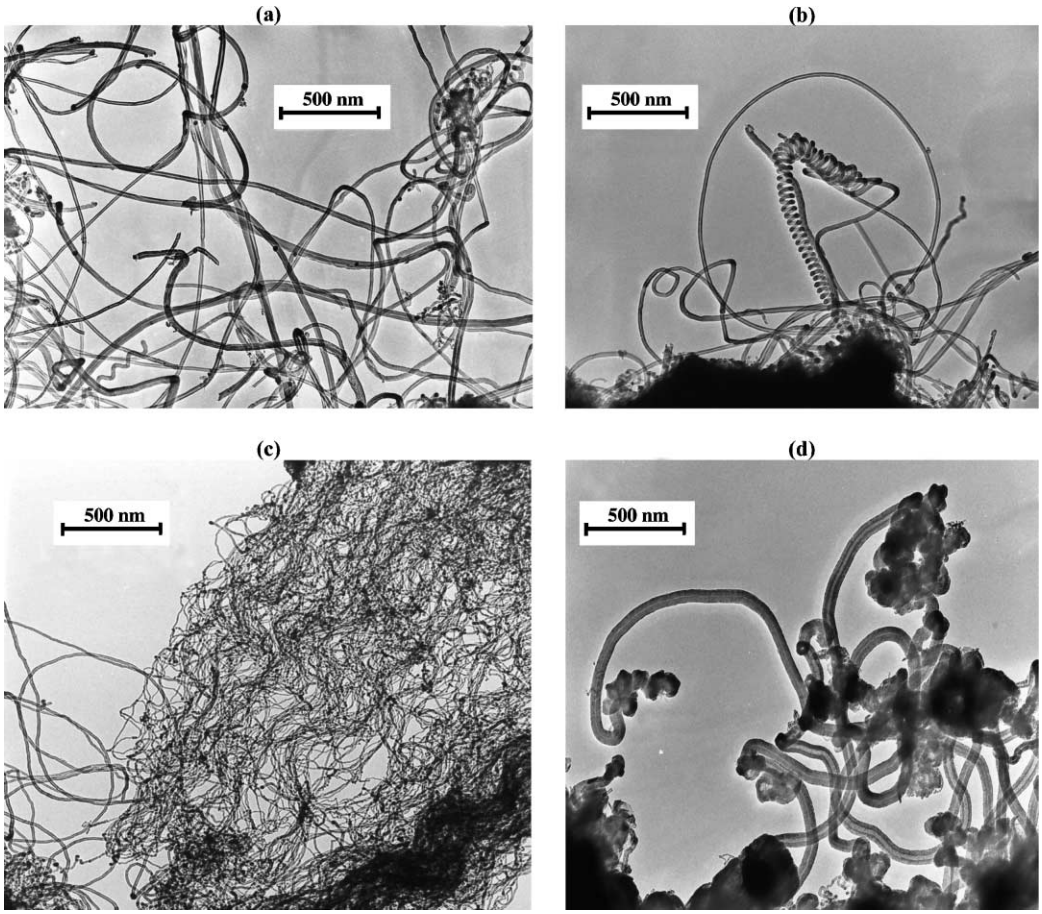

Fig. 1. Low magnification TEM images of NTs obtained by the catalytic decomposition of acetylene over different catalysts: (a) Co–Al_2O_3(P) at 700 °C; (b) Fe–Al_2O_3(P) at 700 °C; (c) Fe/Co–Al_2O_3(P) at 600 °C; (d) Fe/Co–Al_2O_3(C) at 700 °C.

NTs. Several methods of purification of NTs produced by catalytic method have been reported [33,34].

TEM analysis of the carbon deposit indicated four forms of carbon, viz., amorphous carbon on the surface of the catalyst, filaments of amorphous carbon, graphite layers covering metal particles and MWNTs formed from well-crystallized graphite layers (i.e., turbostratic MWNTs). MWNTs are usually more or less covered with amorphous carbon on the outer layer.

3.2. Quality of MWNTs produced on Fe or Co supported catalysts

At 600 °C Fe–Al_2O_3(P) or Co–Al_2O_3(P) formed only a moderate quantity of NTs. Whereas the carbon deposited on Fe–Al_2O_3(C) or Co–Al_2O_3(C) did not contain any carbon tubes, but only amorphous carbon. Nevertheless, the carbon deposit at a N_2 flow of 75 ml/min (Table 1) varies from 15 to 25%. It represents a huge amount of amorphous carbon.

On the other hand, at 700 °C, all the catalysts were found to be active in the production of high density of NTs (Fig. 1a and b). The carbon tubes formed were of different quality, ranging from very thin to thick. High resolution TEM (HRTEM) revealed that the tubes were multi-walled in nature consisting of 5–15 layers. The density of carbon tubes on only Co-containing supports was higher than on only Fe-containing samples.

3.3. Quality of MWNTs produced on Fe and Co supported catalysts

It is interesting to note that when alumina support had a mixture of iron and cobalt, a very high density of NTs was observed even at 600 °C (Fig. 1c). TEM analysis showed that the catalyst grains are uniformly covered by web-like network of MWNT bundles. The density of these bundles was so high that no good representative TEM picture could be taken. An analysis by HRTEM indicated that the nanotubes grown on Fe/Co–Al_2O_3(P) are good in quality as well as quantity. Fe/Co–Al_2O_3(C) also showed the formation of reasonably good quantity of NTs, but these tubes were found to be very thick and covered with a dense outer layer of amorphous carbon (Fig. 1d).

At 700 °C, the NTs produced on Fe/Co–Al_2O_3(P) were of the best quality, i.e. they possessed well-crystallized graphite layers (i.e., turbostratic in nature) with almost no amorphous carbon on their surface. The average inner and outer diameters of these carbon tubes were found to be in the range 5–10 nm. A more detailed explanation to understand the quality of the carbon tubes formed based on the metal–support interaction awaits further investigation.

4. Conclusion

A comparison of catalytic activity of Fe, Co and Fe/Co supported on Al_2O_3 or SiO_2 (supports obtained by different methods) indicated that a best yield of MWNTs is resulted at 700 °C on hydrated alumina prepared from aluminum isopropoxide and containing a mixture of Fe and Co on it. Analysis of the carbon deposit by TEM indicated that catalyst particles are uniformly covered by a web-like network of MWNT bundles. Formation of Fe and Co alloy, within the reducing environment probably assist in homogeneous dispersion of metal particles on the support, resulting in the formation of higher quantities of MWNTs. It may also be added that an effort to correlate the influence of the nature of metal–support interaction with NTs formation is not conclusive, but needs further investigation.

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