

SYNERGISTIC EFFECT OF Ni-Zn BASED CATALYSTS ON THE GROWTH OF CARBON NANOMATERIALS

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ABSTRACT

Carbon nanomaterials were prepared by the chemical vapour deposition (CVD). CVD is an accepted method for production of carbon nanotubes/fibers due to its relative simplicity of operation, process control, energy efficiency, versatility in the use of raw materials, high yield and product purity. The principle of CVD is the decomposition of various hydrocarbons over metal supported catalyst. Nickel and Zinc based mono and bimetallic catalysts were prepared by wet impregnation method. Catalysts were used for the preparation of nanocarbon by CVD method to investigate their synergistic effect. Prepared carbon nanomaterials were characterized by Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), Raman Spectroscopy, Thermal Analysis and Transmission Electron Microscopy (TEM). Diameter of the prepared carbon nanotubes/fibers were observed in the range 40-120 nm under TEM microscopy. Carbon deposition and average growth rate were found maximum for Ni-Zn based silica supported bimetallic catalyst under CVD method.

Keywords: Nanomaterials, Bimetallic catalysts, CVD, SEM, Raman spectroscopy

INTRODUCTION

In the field of materials science, structureproperty-application relationship is an important aspect. Many materials are known for their very unique properties and structural relationship. One of the most versatile materials is carbon and it is interesting to know the relation between its versatility and allotropes. Carbon exists in several allotropes like diamond, graphite and fullerenes [1]. As the structures of allotropes vary, they also have different physical and chemical properties. Research in the field of carbon science is increasing on alarming rate since the discovery of Fullerene in 1985 [2]. all carbon materials, Among carbon nanomaterials attracted much attention from scientific community since last few decades. There are many types of carbon nanomaterials like carbon nanotubes (CNTs). carbon nanofibers (CNFs), carbon nanospheres, graphene etc. Oberlin et al. [3] reported the Chemical Vapour Deposition (CVD) growth of nanofibers (CNFs) carbon by benzene 1991, Iijima decomposition. In reported formation of multiwalled carbon nanotubes (MWNTs) [4]. Two years later singlewalled carbon nanotubes (SWNTs) were synthesized by Iijima and Ichihashi [5] and Bethune et al. [6] with the help of metal catalyst particles. Carbon nanotubes (CNTs) and various types of carbon nanofibers (CNFs) have also drawn increasing attention due to their special properties and potential applications [4,7-9]. The Catalytic Chemical Vapor Deposition (CCVD) method is one of the most powerful techniques for synthesis of CNTs and CNFs, although carbon nanomaterials can be synthesized using various methods including arc discharge and laser vaporization [10]. The morphology and quality of the prepared nanocarbon depends on factors such as (i) selection of catalyst and carbon source, (ii) reduction temperature of the catalyst, (iii) reaction temperature and (iv) nature of catalyst support etc. [11].

The most widely used carbon sources are acetylene, methane, ethylene, ethanol, benzene, xylene and toluene. Due to the thermodynamic properties and chemical structures of the organic molecules, the hydrocarbon intermediates generated on catalyst surface have a significant effect on the morphology of final products [11]. Selection of appropriate catalyst is a major factor for synthesis of carbon nanomaterials through chemical vapour deposition method. For preparation of catalysts, researchers have used various precious metals as well as transition metals on different supports. It is known that Fe, Co and Ni nanoparticles provide centers for carbon nucleation and act as active sites for the decomposition of carbon species [11]. Transition metals, which are widely used as catalyst for growth of carbon nanomaterials, have vacancies in the d-electron orbital and with increasing delectron vacancies they show increasing affinity

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for carbon. Metals without any vacancy in dshells like Zn or Cu has little affinity for carbon [12-14]. It is interesting to investigate behavior of metals like Zn and Cu with other active metals like Fe, Ni for the growth of carbon nanomaterials. In addition of monometallic catalysts, researchers have identified the role of more than one metal i.e. multimetallic catalyst systems for the growth of carbon nanomaterials. Carbon nanotubes were synthesized using Co-Mn, Fe-Co, Fe-Ni, Co-Mo, Fe-Mo, Ni-Co and these catalysts have been found to improve the CNTs growth [15-18].

It was found that supporting a metal or a mixture of metals on different oxides (MgO, SiO₂, Al₂O₃), zeolites, clay would result in enhancement of catalytic activity and ultimately it affects the formation of carbon nanomaterials [19-23]. It is obvious that the optimum interaction between metal and support has a positive effect on the growth of carbon nanostructures. The interactions between a metal and support can be either physical or chemical. Vander Wal et al. [24] reported that, physical interaction between metal and support can be responsible for the size distribution of metal particles.

Catalysts preparation can be done by introduction of metal precursors onto a suitable support and this can be accomplished by several, established methods. Common methods include: (i) impregnation, which involves deposition of a metal precursor onto a support, typically from an aqueous solution (ii) co-precipitation, in which the support and metal precursor are simultaneously precipitated from solution, (iii) ion-exchange, as commonly used for the preparation of zeolite supported catalysts (iv) sol-gel method and (v) physical deposition [25,26]. Each method has its own advantages and disadvantages. Due to simplicity, impregnation is generally used for the preparation of catalysts. Two different modes of impregnation are known and well implemented: wet impregnation and incipient wet impregnation. In wet impregnation, the support material is brought into contact with a solution containing metal precursors. By evaporation of the solvent followed by calcination, the metal is impregnated into the support. In general, the wet impregnation results in the metal being

dispersed inside the pore as well as on the surface of supports.

The role of mono (nickel)/bimetallic (nickel with zinc) system and catalyst support for the growth of carbon nanomaterials is in the center of the present investigation. It is very interesting to check the behaviour of zinc in absence and presence of nickel for nanomaterials growth. For this purpose, different catalysts, supported on both silica (SiO₂) and alumina (γ - Al₂O₃), were prepared using wet-impregnation method. CVD method was used to prepare carbon nanomaterials. Various characterization techniques have been used to investigate nanomaterials properties and their relation with catalytic activity.

EXPERIMENTAL

Preparation of mono and bimetallic catalysts

Metal salts of nickel and zinc were used as metal precursors for the preparation of catalysts which responsible for were the growth of nanomaterials. Better dispersion of metal particles and small particle size are the major challenges for the preparation of suitable catalysts. Supported catalysts are more active catalysts; therefore silica and alumina were used as support to disperse the metal particles. Resultant metal particles on the support surface are the active sites for the growth of carbon nanomaterials. To get better dispersion, wetimpregnation method has been applied to synthesize mono and bimetallic catalysts. $Ni(NO_3)_2 \cdot 6H_2O$ solution and $ZnSO_4 \cdot 7H_2O$ solution were added to SiO_2/γ -Al₂O₃ slurry (made in distilled water) as a support. The mixture was stirred for 3 hours at room temperature and heated to 90°C for 1-2 hours under stirring (until all the water in the mixture evaporated). Then the paste was dried in an oven for 12 hours at temperature of 90°C. The resulting powder was calcined at 550°C for 3 hours. Monometallic catalysts were prepared by same manner, but each metal salt was impregnated separately on SiO₂ support. For monometallic and bimetallic catalysts comparison study, three silica supported catalysts were prepared (10NiSiO₂, 5ZnSiO₂, 10Ni5ZnSiO₂) and for support comparison, bimetallic catalysts on silica and alumina (10Ni5ZnSiO₂, 10Ni5ZnAl₂O₃) were prepared.

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Catalysts code, compositions and other details are presented in Table-1.

CVD set-up

The experimental setup used for the preparation of the carbon nanofibers/tubes is schematically shown in Figure 1. The reactor is made up of 930 mm long quartz tube of 32 mm inner diameter with provisions of inlet of reactants and outlet of spent vapor. The reactor was placed in a tubular electrical furnace. The catalyst was kept in sample holder present in heating zone of the horizontal quartz reactor.

The experimental set-up shown in figure was first flushed with nitrogen gas. The temperature of the heating zone was controlled by programmable temperature controller. Carbonaceous source used for production of carbon nanomaterials was xylene and it was injected using syringe pump. After deposition of carbon under optimized reaction conditions, the vapor/gas was allowed to go out through the gas bubbler to exhaust.

Synthesis of carbon nanomaterials

Quartz boat containing appropriate amount of metal oxide catalyst was kept into reactor. N2 gas was passed through the quartz reactor and simultaneously the temperature increased up to 500°C at the rate of around 2.4°C/min. At the reduction temperature of 500°C, subsequently N_2 was replaced by H_2 with the flow rate of 20 ml/min for 20 minutes to reduce metal oxides and hence it get transformed into active metal particles which can act as a nucleation site for the growth of nanocarbons. Further, temperature was increased at the rate of 2°C/min to 800°C in N₂ atmosphere only. At 800°C, reaction was carried out in presence of N₂ (150 ml/min) and H₂ mixture. Simultaneously, carbon source xylene (analytical grade) was injected at the rate of 0.5 ml/min for 30 min of duration. Due to high temperature in the reactor, xylene was vaporized and decomposed on catalyst. After 30 minutes, H₂ flow was stopped and temperature decreased gradually. Samples were collected after the decreasing of temperature up to room temperature. Carbon deposition and Average growth rate can be calculated using following equations,

Carbon Deposition % = $\frac{Mtotal-Mcatalyst}{Mcatalyst} \times 100$

Average growth rate = $\frac{Mtotal-Mcatalyst}{Total growth time}$

Reaction conditions used in the present study are the suitable conditions which were established well during previous experiments and reported elsewhere [27].

Nanomaterials characterization

Nanomaterials produced by CVD method were different sophisticated characterized bv techniques. Samples were observed under Scanning Electron Microscope (SEM) Hitachi S-3000N to ascertain formation of nano size elongated structures (fibers or tubes). Transmission Electron Microscopic observation was done using Philips (TEM), Tecnai-20. Thermo Gravimetric Analysis (TGA) of carbon materials was carried out up to 800°C on Mettler Thermal Analysis system TA 4000 with TG50 for getting information about amount of catalyst present in the product and also to study oxidation behaviour of carbon nanomaterials. The phases present in the resultant materials were detected using powder X-ray Diffraction (XRD) conducted on a Philips, X-pert MPD. Raman Spectroscopy of carbon samples were performed by Renishaw inVia Raman Microscope.

RESULTS AND DISCUSSION

Nanocarbon deposition

Catalyst preparation for the growth of carbon nanomaterials is crucial. Appropriate choice of metal or combination of different metals can lead the growth rate, but at the same time selection of support can also play a vital role. For the better growth, better dispersion of metal particles on the support is required and optimum metal-support interaction (MSI) improves the catalytic activity. Generally, wet-impregnation method provides the fine and better dispersion of the particles on the suitable support. In this study, two different systems (i) mono and bimetallic metals on same support i.e. SiO₂ and (ii) γ -Al₂O₃ and SiO₂ supports with bimetallic system have been used to investigate the behaviour of different supports. All the catalysts were prepared using wet-impregnation method as discussed in experimental procedure. All reaction conditions were exactly similar as discussed in experimental section. Nanocarbon

was prepared at 800°C temperature, showed black soot like appearance by naked eye. After the reactions, results in the form of carbon deposition and average growth rate are complied in Table-2.

Role of mono and bimetallic catalysts on silica

To investigate the role of each metal on the growth of carbon nanomaterials and synergistic effect of metals, three different catalysts of Ni, Zn, Ni:Zn on SiO₂ support (Table-1 and 2) were used. First, monometallic catalyst of 10 wt.% Ni on SiO₂ was used for chemical vapor deposition process and it showed 50.62% of carbon deposition. To check the activity of only Zinc, monometallic sample of 5 wt. % Zn on silica was used for CVD under similar conditions and it showed very less amount of carbon deposition i.e. 4.96%. Zinc has no d-vacancies in their electron configuration so it exhibits a negligible affinity for carbon [12-14]. To find out the specific role of Zn with Ni, silica supported bimetallic catalyst with 10 wt.% Ni and 5 wt.% Zn was placed in CVD chamber under the similar reaction conditions, and 104.96% of carbon deposition was found (Figure 2). It is revealed that zinc is acting as a promoter with nickel as main metal for the growth of carbon nanomaterials. In the case of bimetallic catalyst (Ni:Zn), more carbon deposition occurred due to Zn might be helping Ni for better dispersion than monometallic (only Ni) on silica and as a result carbon deposition rate is faster in bimetallic system. In addition, there may be possibility to prevent aggregation of catalyst particles in the case of Ni:Zn system. From this study, we can say that deposition of a carbon material and average growth rate over silica supported bimetallic catalyst are higher than monometallic due to synergistic effect of Ni:Zn particles i.e. 10Ni5ZnSiO₂>10NiSiO₂>5ZnSiO₂ (Fig. 2).

Effect of support in bimetallic catalysts

Figure 3 shows relation between carbon deposition and type of support in the case of bimetallic catalysts i.e. 10Ni5ZnSiO₂ and 10Ni5ZnAl₂O₃. To find out the effect of support, Ni:Zn based silica and alumina supported catalysts were used for CVD reaction under similar conditions as applied in mono and bimetallic study, explained previously. Catalytic

activity is the major concern for the growth of carbon nanomaterials, especially in CVD method. Dispersion of active metal particles, nature of support, metal-support interaction, catalytic activities are main characteristics and they are interrelated with each other. Silica and alumina are well known conventional supports. albeit their compatibility with different metals to get higher yield is still required further study. As seen in figure 3, the maximum carbon yield can be achieved in silica supported catalyst. Experimental results show that average growth rate of nanomaterials is also better on silica catalyst than alumina catalyst (Table-2). When the support is a metal oxide, oxidation/reduction reactions occur through the transfer of an oxygen atom from support to metal and vice versa. Acid/base interactions are depending on the Lewis acid and base characteristics of the materials. In the cases of metal oxides, surface anions act as Lewis base sites (electron pair donor) and cations as Lewis acid sites (electron pair acceptor) [24]. The nature of the catalysts depends on the interaction between metal and its support, therefore nature of catalysts is a key feature associated with the dispersion of the metal on its support. In the present study, there is a possibility of less active area of metal particles available on alumina and it resulted in smaller amount of carbon deposition occurred than on silica catalyst.

Nanocarbon characterizations

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM)

Prepared samples were viewed under Scanning Electron Microscope (Hitachi S-3000N). Figure 4 displays SEM micrographs of carbon nanomaterials grown over metallic catalysts having lengths in the range of several micrometers. It also shows the morphology of the catalysts which provide nucleation sites for the growth of nanomaterials. Nanomaterials were grown by the diffusion of carbon through a metal catalyst and its subsequent precipitation as carbon products in various shapes. Growth of carbon in the shape of fibers/tubes can be seen in Ni containing mono and bimetallic catalysts (10NiSiO₂ and 10Ni5ZnSiO₂, Fig. 4a and 4c). In of 10ZnSiO₂ and $10Ni5ZnAl_2O_3$. case formations of carbon fibers are not observed. In these cases catalysts are surrounded by carbon Maximum carbon aggregates. materials

deposition can be clearly observed in 10Ni5ZnSiO₂ bimetallic catalyst.

In Figure 5, it is observed that carbon deposited in the form of fibers on bimetallic sample (10Ni5ZnSiO₂) which was viewed under Transmission Electron Microscope. The long carbon fibrous nanostructures were observed under TEM analysis (Figure 5). The produced fibers/tubes show similar and unusual throughout the sample. morphology The resultant fibers/tubes have dimension between 40 nm to 120 nm. As seen in the images, it is revealed that elongated structures of about 100 nm dimensions and entangled with each other.

X-ray diffraction (XRD)

XRD is used in order to ascertain the quality and crystalline nature carbon materials. From the XRD pattern of carbon deposited on silica supported catalyst (Figure 6), the characteristic peaks for carbon can be seen at 2θ positions of 26.22° and 44.50°, which are attributed to (002) and (101) reflections respectively ((JCPDS card No. 75-1621). Peaks at 44.50° and 51.90°(2θ) corresponds to Ni are also presented in diffractogram (JCPDS card No. 65-0380). Carbon deposited on nickel catalysts is also confirmed by XRD results.

Thermo gravimetric analysis (TGA)

TGA of carbon materials was carried out using Mettler Thermal Analysis system TA 4000 with TG50 for getting information about amount of catalyst present in the product and also to study oxidation behaviour of carbon nanotubes. TGA of carbon materials was carried out in presence of air with heating rate 15 °C /min up to 800°C.

Figure 7 shows TGA graph of carbon nanomaterials obtained from xylene on $10Ni5ZnSiO_2$. Nanocarbon prepared on Ni:Zn based catalyst at $800^{\circ}C$ exhibits higher oxidation initiation temperature (560°C), thereby indicating that this carbon material have good thermal stability. It is known that crystalline carbon exhibits oxidation at higher temperatures than amorphous carbon. Single step weight loss is indication of one type of carbon form present in the material i.e. carbon nanomaterials.

Raman spectroscopy

Raman spectroscopy is commonly used to characterize nanomaterials. It reflects different

characteristic spectra for sp³, sp², and sp carbons, as well as for disordered sp^2 . The Raman spectrum was taken using a 514 nm Argon Laser excitation wavelength. The first order Raman spectrum is composed of two main peaks, at 1350 cm⁻¹ and 1580 cm⁻¹, which are assigned as the disorder (D band) and graphite band (G band), respectively [28]. Figure 8 shows Raman spectra results of carbon prepared on mono and bimetallic catalysts. It attributes the presence of D-band and G-band. The calculated ratio of the integrated intensity of the D and G peaks, $R_I = I_D/I_G$, characterizes the disorder in the carbon nanomaterials. R_I=0.66 is for 10NiSiO₂, R_I=0.73 for 5ZnSiO₂, R_I=0.89 for 10Ni5ZnSiO₂ and R₁=0.81 for 10Ni5ZnAl₂O₃. Therefore, it can be predicted from the calculation that fibrous carbon deposited on nickel supported silica is more crystalline in nature than the other catalyst systems.

CONCLUSIONS

Carbon nanomaterials were grown by CVD method using Ni and Zn based monometallic and bimetallic catalysts. The morphology and growth were found to be dependent on the type of catalyst and combination of metals as well as support system (silica and alumina). SEM and TEM micrographs showed that Ni and Ni-Zn based silica catalysts were suitable to grow carbon tubes/fibers among all four catalysts systems, where as fiber formation was not observed in case of Zn-based monometallic silica catalyst. Furthermore, the combination of Zinc and Nickel makes a significant difference in catalyst activity and responsible to finalize the shape of carbon deposition. The growth of carbon products were observed higher in silica supported bimetallic catalyst (10Ni5ZnSiO₂) than the monometallic catalyst systems. The presence of Zn and Ni on silica support have influenced structure, carbon deposition and average growth rate of carbon materials, whilst the catalyst prepared with Zn and Ni on alumina support resulted in lower carbon deposition than silica bimetallic catalyst. No fiber formation was observed on alumina catalyst. In the present investigation, silica supported catalysts were found better than alumina supported catalyst in terms of catalytic activity and formation of carbon nanomaterials.

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Catalyst	Ni	Zn	RPM	Resultant mass of	Calcination
Code	loading	loading	(Stirring)	prepared	temperature
	wt. (%)	wt. (%)		catalysts	(°C)
				(gm)	
10NiSiO ₂	10	-	300	4.14	550
5ZnSiO ₂	-	5	300	4.89	550
10Ni5ZnSiO ₂	10	5	300	5.11	550
10Ni5ZnAl ₂ O ₃	10	5	300	4.75	550

Table-1 : Catalysts code and conditions used for the preparation of catalysts

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1 9 h l 0 - 7 •	Weight	norcontago of	donocitod	carnon ai	na gvorgao	growth	rate of 1	nrongrod	carnon
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Catalyst	Metal	Support	Reaction	Carbon	Average growth
code	present		temperature	deposition	rate (mg/min)
			(°C)	(%)	
10NiSiO ₂	Only Ni	SiO ₂	800	50.62	0.27
5ZnSiO ₂	Only Zn	SiO ₂	800	4.96	0.02
10Ni5ZnSiO ₂	Ni and Zn	SiO ₂	800	104.96	0.56
10Ni5ZnAl ₂ O ₃	Ni and Zn	Al ₂ O ₃	800	40.37	0.21



Figure 1 : Schematic diagram of CVD set-up

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Figure 2 : Effect of metal on carbon deposition



Figure 3 : Effect of support on carbon deposition



Figure 4 : SEM images of (a) 10NiSiO₂ (b) 5ZnSiO₂ (c) 10Ni5ZnSiO₂ (d) 10Ni5ZnAl₂O₃



Figure 5 : TEM images of 10Ni5ZnSiO₂



Figure 6 : X-ray diffractogram of carbon on silica supported catalyst





Figure 8 : Raman spectroscopy of (a) 10NiSiO₂ (b) 5ZnSiO₂ (c) 10Ni5ZnSiO₂ (d) 10Ni5ZnAl₂O₃