Synthesis of High Purity Carbon Nano Fibers and Hydrogen from Propane Decomposition

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High purity carbon nano fibers/tubes (CNF/Ts) which contain 97% pure graphitic carbon are prepared by a new catalytic method. These carbon nano fibers/tubes are ready to use without any further purification. The striking feature of this method is the production of carbon nano fibers/tubes of narrow distribution range. The developed catalytic method also produces pure hydrogen. An additional advantage of this catalytic method is that catalyst can be reused without reactivation. Ni:Cu catalyst system is embodied into SCHOTT-DURAN filter disc of large pore size (40-100 μm). Due to the production of hydrogen in the reaction catalyst stability is enhanced and deactivation process is considerably slowed down.

Key Words : Propane decomposition. Supported catalyst. Nanocarbons, CO_x free hydrogen

Introduction

Carbon fibers/single walled carbon nanotubes possess vast applications in industries and other fields. However, the preparation of high purity carbon materials is still a challenge for researchers. Today it is a two-step process: carbon fibers/tubes produced in the first step are purified in the second step by treating with strong acids. In the purification process shape and phase of carbon are disturbed which has a direct effect on the physical/chemical/electronic properties of prepared materials. High purity means that the material should be free from carbonaceous deposits and no catalyst particles should remain embodied in the material geometry. Also the consistent diameter of prepared carbon material is very important because it dictates the properties of the material. To prepare a catalyst with uniform particle size is also an area of growing research which is the key for the production of uniform size carbon tubes. This has direct effect on the measurement of energy gaps of semiconducting CNTs and smooth flow of electrons without any dip during optical properties measurements. Preparing narrow gap catalyst particles and CNTs is not trivial and very time consuming.[1-15]

CVD (chemical vapor deposition) is the technique employed to produce such type of geometry. but it requires a solid substrate on which carbon nanotubes can be grown. Recently Endo *et al.*[16] reported the synthesis of more than 95% pure CNTs by methane CVD method with conditioning catalyst and a two step purification process.

In this report we present a simple catalyst method with narrow particle size distribution and growth of high purity CNTs in a single step. ready to use without purification.

Experimental

In this process SCHOTT-DURAN filter disc was impreg-
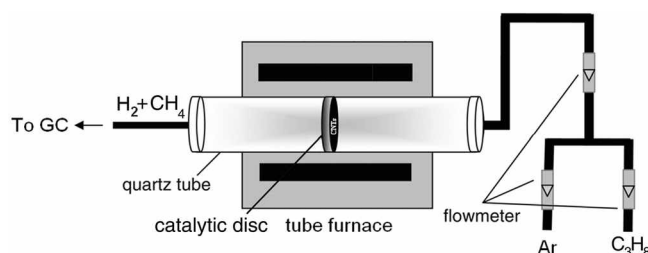

Figure 1. Experimental arrangement for the catalytic production of CNF/Ts by Propane decomposition.

nated with Ni:Cu particles and calcined at 600 °C for 6 hours. The experimental arrangement is presented in Figure 1.

The process involves the preparation of solution of copper and nickel from their respective nitrate salts with final concentration of nickel being 25% and that of copper 3%. Nickel and copper concentrations in the final product were analyzed using Atomic Absorption Spectroscopy and found to be 24.1% and 2.78% respectively.

The experiment of propane decomposition was performed at 673 K and at atmospheric pressure. which is low in comparison with the other catalytic processes used to-date for the production of CNT/Fs.[17,18] 97% pure CNTs are produced along with CO_x free hydrogen in accordance with the following chemical reaction

$$C_3H_8 \xrightarrow{\text{Catalyst Bed}} 2C + CH_4 + 2H_2$$
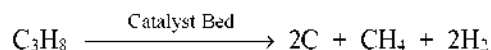
This hydrogen can be used directly in the fuel cell system without any purification. The hydrogen produced regenerates the catalyst within the reaction thus catalyst stability is enhanced and the reaction proceeds for 300-400 hours with continuous formation of carbon and production of hydrogen.

Results and Discussion

The nanotubes grown at the surface of SCHOTT-DURAN filter disc were removed and analyzed by XPS/SEM and the particle size measurements. SEM samples were dispersed on Silver paint and XPS samples were analyzed using a specifically built powder sample holder.

SEM image of the CNTs sample after the propane decomposition reaction is shown in Figure 2.

Particle size analysis is performed using FRITSCH Analysette 22 equipment and presented in Figure 3.

Figure 4 presents the XRD analysis of the supporting discs before Ni:Cu impregnation. after Ni:Cu impregnation and CNTs produced after the catalytic decomposition of pro-
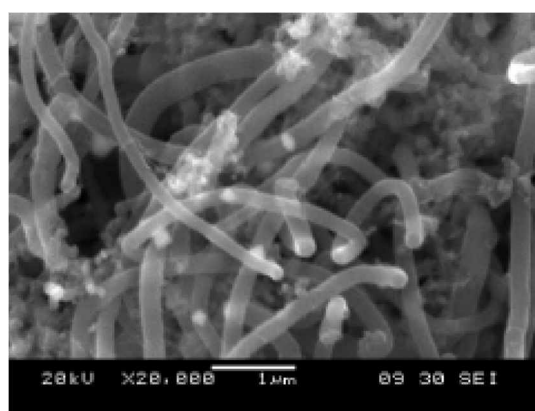

Figure 2. SEM image of carbon nanotubes grown from catalytic propane decomposition.
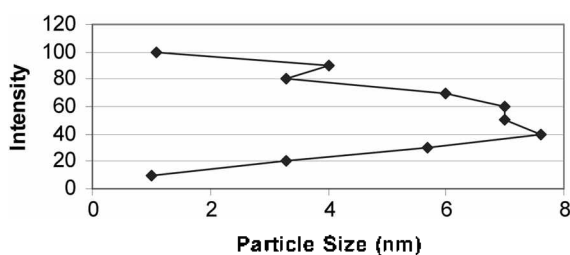

Figure 3. Diameter distribution of CNTs.

pane. The XRD results clearly indicate good graphitization (95-97%) of CNTs. These results show that substantially pure form of graphitic carbon can be produced by the modified catalyst used in this study. XPS study reported in Figure 5(a) supports the XRD findings: pure from of graphitic carbon (97.6%) is formed. It is concluded that our CNTs have good graphitic properties in comparison with the other methods used. This is a single step process and CNTs produced can be used without any further purification.[19-22]

Examination of particle size data revealed that the average diameter of CNTs was around 7.5 ± 0.5 nm (Figure 3).

Catalytic studies of Ni:Cu/disc showed that this catalyst can be very effective for the growth of CNTs and production of pure hydrogen. Online GC/MS analysis revealed only hydrogen. methane and unreacted propane in the products. The catalyst conversion was estimated from the propane conversion and it comes out to be around 70%. This. we propose. is due to the modified method of preparation of catalyst which has a Ni dispersion of more than 60% as ascertained from CO-chemisorotion experiment presented in Table 1.

Due to high dispersion of active metal on the surface the catalyst activity towards the decomposition of propane is enhanced. this is due to the presence of different ionic states of nickel and copper on the surface as presented in Figure 5
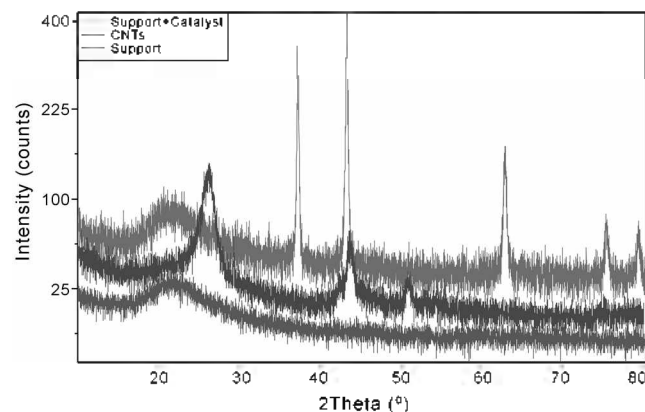

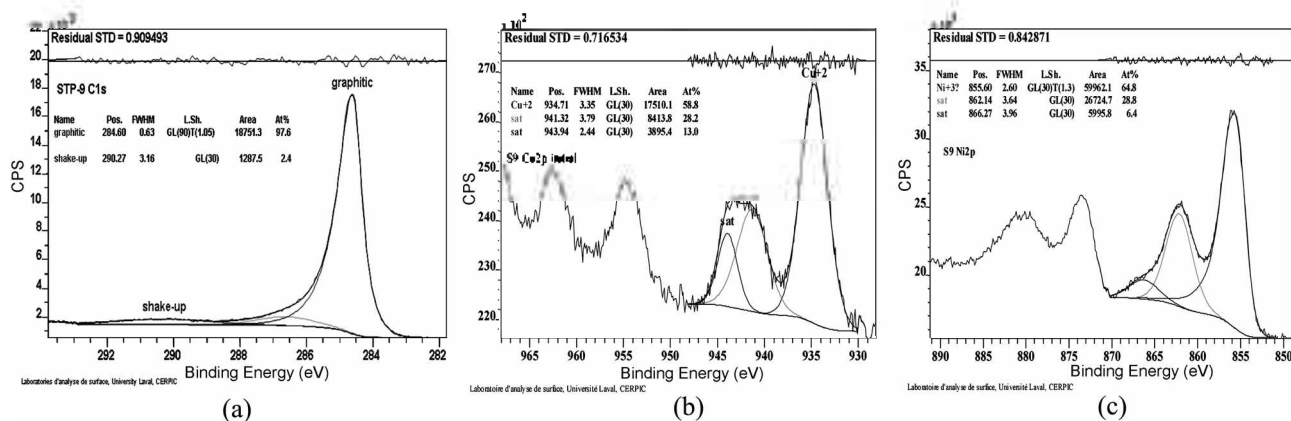**Figure 4.** XRD analysis of pure SCHOTT-DURAN filter disc, Ni:Cu/disc catalyst and CNTs.

Figure 5. (a-c) Formation of pure graphitic carbon, change in Cu and Ni oxidation state during decomposition of Propane over Ni:Cu/disc catalyst.

Table 1. Co-chemisorption analysis of Ni:Cu/disc modified catalyst

Catalyst Designation	CO-chemisorption ($\mu mol/g$)	% Dispersion (Ni)
Ni:Cu/disc	0.967	60.23
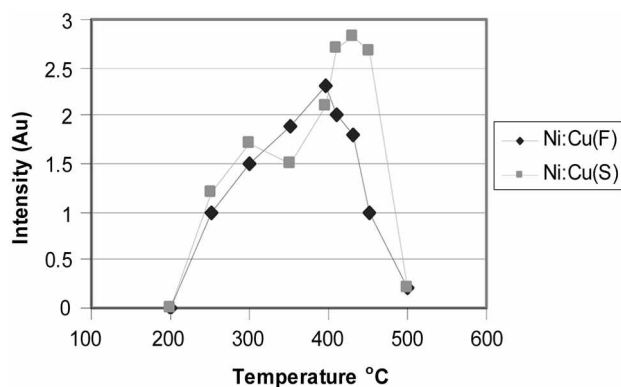
Figure 6. TPR analysis of Ni:Cu/disc (Fresh) and Ni:Cu/disc (Spent) catalysts.

(b & c).

TPR analysis of fresh and spent catalysts presented in Figure (6) shows that only one peak appeared at 450 °C which belongs to Ni:Cu, this peak is shifted to lower temperature on the spent catalyst (397 °C) and two other peaks appear at 410 and 430 °C which correspond to different ionic states of Cu and Ni. The striking feature is that no metal support interaction takes place between the support and Ni:Cu. The humps produced in between the two peaks on spent catalyst are due to the presence of different oxidation states of Ni and Cu. The TRR studies clearly indicate that dispersion of Ni and Cu on the surface of the catalyst is quite high.

We believe that more carbonaceous deposits are formed during the catalytic reaction when higher oxidation states of Ni and Cu are present at the reaction temperature. A series of experiments revealed that higher reaction temperature de-

Table 2. Positive and negative ions spectra of the catalyst

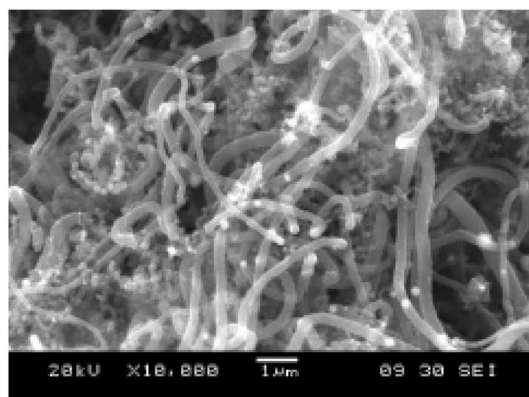| Ion	amu	Ion	amu
$^{63}Cu^{58}Ni$	120.8911	^{65}Cu	64.9270
Ni_2Cu	180.8524	$^{63}Cu^{58}Ni$	120.8911
$NiCu_2$	186.0012	Ni_2Cu	180.8524
Ni_3Cu	238.7707	$NiCu_2$	185.9825
Ni_2Cu_2	244.0265	Ni_3Cu	239.0318
$NiCu_3$	248.9967	Ni_2Cu_2	244.0265
Ni_3Cu_2	301.1647	$NiCu_3$	249.0910
Ni_3Cu_2	302.1824	Ni_3Cu_2	301.1647
Ni_2Cu_3	307.1037	Ni_3Cu_2	302.1824
$NiCu_4$	311.0455	Ni_2Cu_3	306.8098
Ni_4Cu_2	361.2757	$NiCu_4$	310.9101
Ni_2Cu_4	371.2176	Ni_4Cu_2	361.2824
Ni_3Cu_4	429.2697	Ni_2Cu_4	371.2176
		Ni_3Cu_4	429.2697

creases the purity and production of CNTs due to the reason that at high temperature particles' agglomeration occurred due to the conversion of Ni:Cu bimetallic, this results in decrease in the product selectivity and catalyst activity also. Non-homogeneous distribution of Ni:Cu on filter disc may be responsible for this change. Also it is revealed that catalysts with higher concentrations of Ni and Cu (> 25% and > 3% respectively) on support disc do not yield pure form of CNTs and highest reduction temperatures are observed for 25%Ni:3%Cu catalyst. This suggests that lower ionic states of Ni and Cu can only be achieved at the 25%Ni and 3%Cu dispersion. The Secondary Ion Mass Spectrometry analysis of the catalyst, in its static mode (+ ve and −ve), is presented in Table 2.

Results indicate the transformation of surface and development of new surface active sites. these surface sites are mainly responsible not only in production of pure form of graphitic carbon but also in the production of CO_x free hydrogen. This is pioneer study which has been conducted in this area and maps the whole surface of the catalyst during the catalytic reaction. Studying this table we can argue the formation of bimetallic/trimetallic species which hinder the formation of CO and CO_2 by the addition of Cu and produce hydrogen which can be directly used in the fuel cell system without further purification.

As the valence state of nickel and copper is increased during the reaction, new site is generated which goes at the highest orbital levels. Since the catalyst particles are in the nano range, consequently tremendous amount of energy is generated during the reaction. During the catalytic decomposition of propane different oxidation states of Ni and Cu are formed which simultaneously reduce to Ni and Cu metallic states because of the production of hydrogen during the reaction. This results in better catalyst stability. Propane decomposes to lower hydrocarbons and decomposition of these hydrocarbons also adds in the production of CNTs. The Raman data of the raw CNTs sample also confirms the importance of different Ni and Cu ionic states. The G/D ratio of CNTs sample synthesized using higher Nickel concentration, without formation of enough Ni and Cu ionic states, was 6.78 while the G/D ratio of CNTs from 25%Ni:3%Cu sample was 13.1. The increase in G/D ratio suggests that

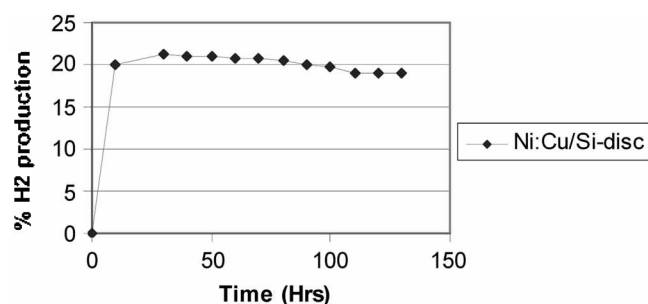**Figure 7.** Bundles of CNTs grown from propane decomposition.

Figure 8. Hydrogen production for the decomposition of propane over Ni:Cu/disc catalyst.

CNTs of high purity were obtained.

Figure 7 presents bundles of CNTs of same dimensions. One possible explanation is that these bundles are grown during the catalytic reaction from the closely positioned nickel particles formed on a certain lattice factets of Ni:Cu which produce CNTs of similar dimensions, this argument is supported by our CO-chemisorption studies where Ni dispersion was reported very high. This results in increase in the nucleation efficiency of Ni:Cu nano particles in comparison with agglomerated particles.

In summary we demonstrated that Ni:Cu/disc catalyst produces high purity CNTs of similar dimensions and CO_x free hydrogen due to the formation of different ionic species of Ni and Cu during the reaction. The effect of particle size also demonstrates the effect on CNTs production. These CNTs can be employed for further studies without purification. The CNTs production reaction can be performed continuously for 100-120 hours. After 120 hours CNTs are recovered and the same Ni:Cu/disc can be used further without any treatment to the catalyst for another 100-120 hours. Figure 8 presents the production of hydrogen with time for the decomposition of propane, which clearly shows the stability of the catalyst for this type of reaction.

Conclusions

1. A heterogeneous layer of Ni and Cu in very close vicinity is produced on the surface with very narrow particle size range.

2. The ionic states of Ni and Cu nano particles catalyse the growth of CNTs.

3. Simultaneous production of hydrogen helps in regener-

ation of catalyst. thus production of CNTs increases with the catalyst stability.

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