Kasetsart J. (Nat. Sci.) 35 : 354 - 359 (2001)

Preparation of Carbon Nanotubes by Nickel Catalyzed Decomposition of Liquefied Petroleum Gas (LPG)

Apisit Songsasen and Paranchai Pairgreethaves

ABSTRACT

A method is proposed for the preparation of carbon nanotubes by means of decomposition of liquefied petroleum gas (LPG) using zeolite-supporting nickel as catalyst. The catalyst was prepared by deposition-precipitation method. The carbon nanotubes, which observed by Raman spectrometer and transmission electron microscope (TEM), are approximately 30 nm in diameter and 300-600 nm long. The reaction temperature and the LPG:H_2 ratio have an effect on the amount of carbon nanotubes formed. The highest amount of carbon nanotubes was obtained by using LPG:H_2 ratio of 9:1, the reaction temperature of 1,100°C and the reaction time of 2 hours.

Key words: carbon nanotubes, nickel catalyst, decomposition of LPG.

INTRODUCTION

Carbon nanotubes have increasingly been studied in recent years owing to their important properties and a wide variety of potential applications. The carbon nanotubes may be used, for example, as catalyst support or semiconductor (Ajayan *et al*., 1995; Eric *et al*., 1996; Lago *et al*., 1995; Sloan *et al*., 1997). Three main methods are currently used for synthesis of carbon nanotubes, *i.e.* carbon arc synthesis; chemical vapor deposition (CVD) or catalyzed decomposition of hydrocarbon; and ion bombardment (Ebbesen, 1994). The general reaction for catalyzed decomposition of hydrocarbon, such as methane, may be written as follows:

$$CH_4 + H_2 \xrightarrow{\text{catalyst}} C + 3H_2 \quad \text{....... (1)}$$

The catalyzed decomposition of methane at 600°C using $MgNiO_2$ as catalyst (Cui *et al*. 1999), and the catalytic pyrolysis of benzene at 1200°C using ferrocene as catalyst (Cheng *et al*. 1998) gave carbon nanotubes on a large scale.

In this letter we report the preparation of carbon nanotubes using zeolite-supporting nickel as catalyst and LPG as the carbon source. The effects of the reaction temperature and the LPG:H_2 ratio on the amount of carbon nanotubes formed had also been investigated.

MATERIALS AND METHOD

Preparation of Zeolite-supporting Nickel Catalyst

The catalyst was obtained by deposition-precipitation method, using $Ni(NO_3)_2$•$6H_2O$ (May and Baker No.2725) as starting nickel compound and $NaHCO_3$ (Unilab No.F8K440) as precipitating agent. Zeolite (Fluka No.96096) 36 g was suspended in a 170-cm^3 aqueous solution of 0.4M $Ni(NO_3)_2$ with constant stirring at 1,100 rpm. A 136-cm^3 aqueous solution of 0.8M $NaHCO_3$ was added to

---

Department of Chemistry, Faculty of Science, Kasetsart University, Bangkok 10900. Thailand.

the suspension at room temperature, and the slurry was stirred for 3 hours. The precipitate was filtered, washed with water, and then dried for 23 hours at 383 K, followed by calcination of the precipitate under air for 6 hours at 723 K. The catalyst obtained was characterized by X-ray diffractometer, XRD (Phillips X'pert).

Preparation of Carbon Nanotubes

A 30-cm long stainless steel tube reactor (3/4 inch in diameter) was located in a furnace as illustrated in Figure 1. Zeolite-supporting nickel catalyst 100 mg was placed in the middle of the reactor tube. Nitrogen gas was flown through the reactor in order to flush out any gases inside and to prevent the entering of gases from outside. The reaction was carried out at various temperatures of 500, 600, 700, 800, 900, 1,000, and 1,100°C. The volume ratio of LPG:H_2 was varied: 1:9, 3:7, 5:5, 7:3, and 9:1, with the total flow rate of the LPG-H_2 at 100 ml/min. The reaction time was varied: 30, 60, 90, 120, 150, 180, 210, and 240 minutes. The reaction was quenched by replacing the LPG-H_2 with N_2. The carbon nanotubes were separated from the nickel catalyst by dissolving the product in 40% HF solution. The nanotubes were characterized by Raman spectrometer (RENISHAW, System 2000) using argon laser source, and by transmission electron microscope, TEM (JEOL, JEM1220).

RESULTS AND DISCUSSION

The X-ray powder diffraction (XPD) spectrum of the zeolite-supporting nickel catalyst is shown in Figure 2. This spectrum shows 36 peaks at 16.20, 17.98, 19.21, 20.76, 21.39, 22.56, 23.18, 23.72, 25.08, 25.94, 26.03, 26.87, 27.15, 27.84, 28.34, 29.63, 30.05, 30.71, 31.24, 31.72, 32.46, 33.70, 34.59, 35.05, 36.21, 39.25, 41.77, 42.71, 44.16, 47.69, 48.91, 50.83, 53.24, 61.43, 62.04 and 63.33 degrees, which indicated the presence of zeolite in the catalyst. This spectrum also shows 3 peaks at 37.37, 43.50 and 62.67 degrees, which indicated the presence of NiO (Schmahl *et al.*, 1964).

The catalyzed decomposition product was confirmed to be carbon via the characteristic peaks displayed in the Raman spectrum, Figure 3. A sharp peak at 1580 cm^{-1} and a broad weak peak at 1350 cm^{-1} indicate the sp^2 and sp^3 hybridization of carbon, respectively (Dresselhaus *et al.*, 1995).

The products obtained were mainly carbon

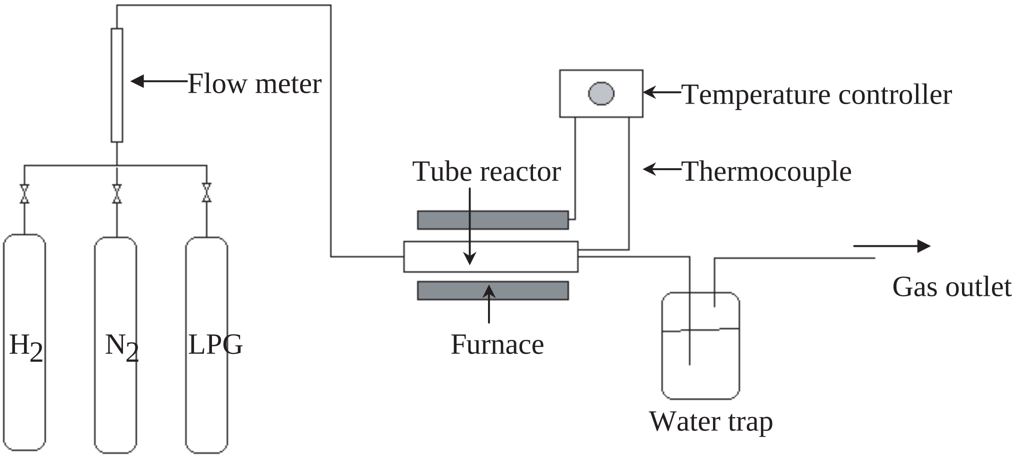

Figure 1 Schematic diagram of the apparatus used for the preparation of carbon nanotubes.

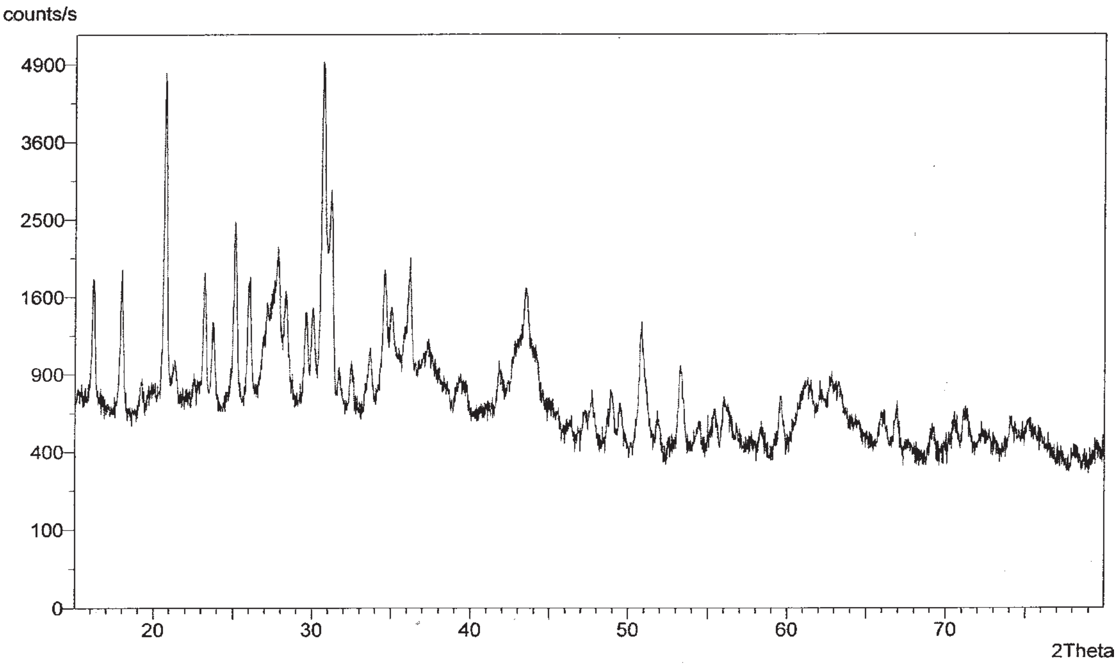

Figure 2 X-ray powder diffraction (XPD) spectrum of the zeolite-supporting nickel catalyst.

nanotubes when the reaction was carried out at 1,000°C and the LPG:H_2 ratio was 3:7. The transmission electron micrographs in Figure 4a and Figure 4b and 4c show the carbon nanotubes before and after being separated from the nickel catalyst, respectively. The nanotubes obtained were single-wall carbon nanotubes of approximately 30 nm in diameter and 300-600 nm long.

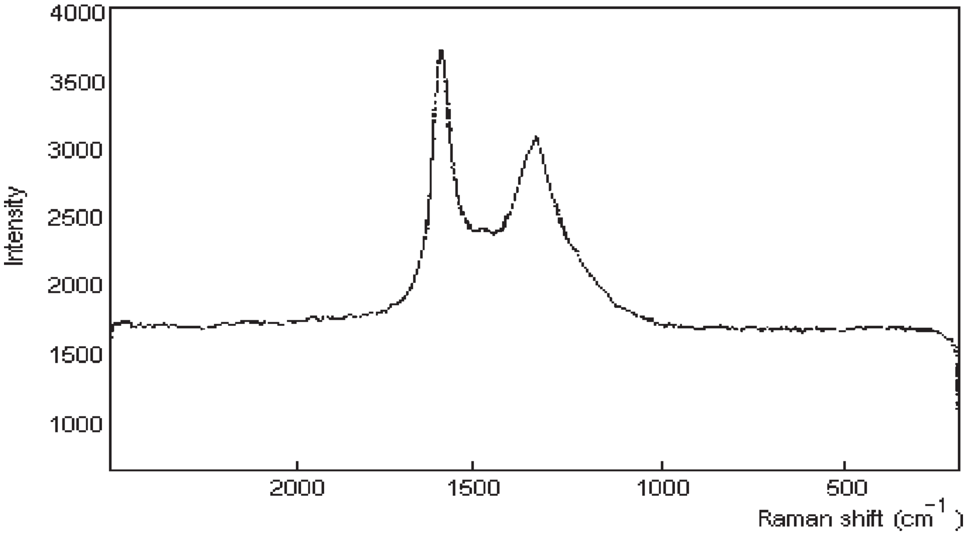

Figure 3 Raman spectrum of the carbon nanotubes.

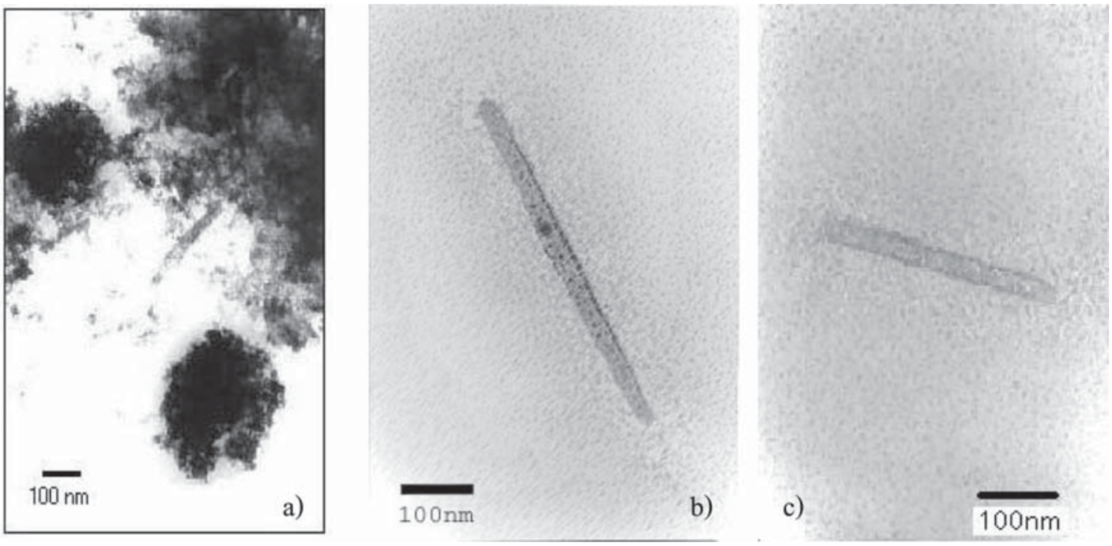

Figure 4 Transmission electron micrographs.
(a) Carbon nanotubes before being separated from Ni catalyst.
(b) and (c) Carbon nanotubes after being separated from Ni catalyst.

Effect of LPG:H_2 ratio on the production of carbon nanotubes

The carbon nanotubes were produced at 1,100°C. The amount of nickel catalyst was 100 mg and the reaction time was 2 hours. The LPG:H_2 ratio was varied as 1:9, 3:7, 5:5, 7:3 and 9:1, and the total flow rate was 100 ml/min. In this experiment, the amount of carbon nanotubes formed increases with the increase of LPG:H_2 ratio as shown in Figure 5. This may be because the quantities of H_2 have an effect on the diffusion of carbon species, which decompose from LPG, into the nickel catalyst. At the low LPG:H_2 ratio (the large quantities of H_2), the rate of carbon diffusion into the bulk (apart

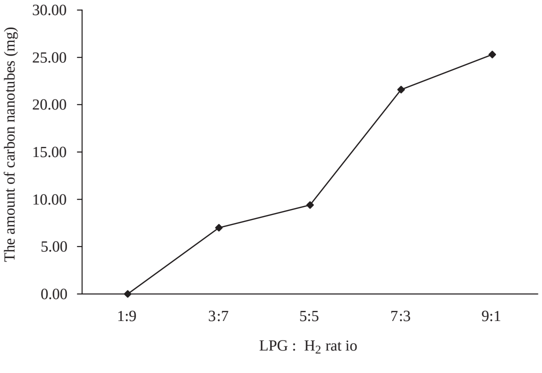

Figure 5 The effect of the LPG:H_2 ratio on the production of carbon nanotubes. (reaction temperature = 1,100°C, reaction time = 2 hours)

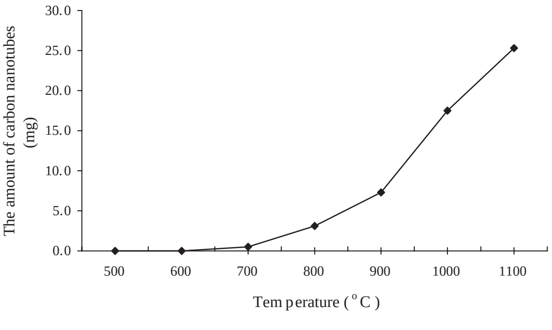

Figure 6 The effect of temperature on the production of carbon nanotubes. (LPG:H_2 = 9:1 , reaction time = 2 hours)

from the nickel catalyst) may be faster than the rate of carbon growth on nickel catalyst, so small amount of carbon can be formed.

Effect of temperature on the production of carbon nanotubes

The carbon nanotubes were produced by using LPG:H_2 ratio of 9:1, and the total flow rate was 100 ml/min. The amount of nickel catalyst was 100 mg and the reaction time was 2 hours. The temperature was varied as 500, 600, 700, 800, 900, 1,000 and 1,100°C. In this experiment, the amount of carbon nanotubes formed increased with increase of the reaction temperature as shown in Figure 6. This may be because the reaction temperature had an effect on the decomposition of LPG. When the reaction temperature was higher, the LPG may be decomposed easier and many carbon species can be formed, so the amount of carbon nanotubes can be greatly increased. In this experiment, we could not prepare the carbon nanotubes at temperature above 1,100°C because the furnace has maximum temperature at 1,200°C.

Effect of reaction time on the production of carbon nanotubes

The carbon nanotubes were produced at 1,100°C by using LPG:H_2 ratio of 9:1, and the total flow rate was 100 ml/min. The amount of nickel catalyst was 100 mg. The reaction times were varied as 30, 60, 90, 120, 150, 180, 210, and 240 minutes. In this experiment, the amount of carbon nanotubes formed was almost constant (about 20 mg) with increase of the reaction time as shown in Figure 7. This may be due to the limitation of catalyst active site, used for the carbon growth.

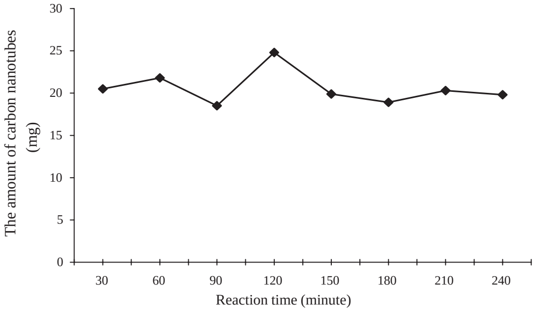

Figure 7 The effect of reaction time on the production of carbon nanotubes. (reaction temperature = 1,100°C, LPG:H_2 = 9:1)

CONCLUSION

The catalyzed decomposition of hydrocarbon using zeolite-supporting nickel catalyst and liquefied petroleum gas (LPG) can prepare carbon nanotubes, which have approximately 30 nm in diameter and 300-600 nm long. The amount of carbon nanotubes formed increases with the increase of the reaction temperature and the LPG:H_2 ratio. The method proposed can be adopted to prepare carbon nanotubes at yield was obtained by using LPG:H_2 ratio of 9:1 at the reaction temperature of 1,100°C and the reaction time of 2 hours. If the conditions are improved further, the yield of carbon nanotubes may be raised to a higher level.

ACKNOWLEDGEMENT

We would like to thank Dr.Pornpan Pornsilapatip, Mrs. Urai Suwanwong, Postgraduate Education and Research Programs in Physical Chemistry, and Department of Chemistry, Faculty of Science, Kasetsart University.

LITERATURE CITED

Ajayan, P.M., C. Stephan, and P. Redlich. 1995. Carbon nanotube as removable templates for metal-oxide nanocomposites and nanostructures. Nature. 375 : 564-567.

Cui, S., C.Z. Lu, and L. Qiao. 1999. Large-scale preparation of carbon nanotubes by nickel catalyzed decomposition of methane at 600°C. Carbon. 37 : 2070-2073.

Cheng, H.M., F. Li, and G. Su. 1998. Large-scale and low-cost synthesis of single-walled carbon nanotubes by the catalytic pyrolysis of hydrocarbon. Applied Physic Letters. 72 : 3282-3284.

Dresselhaus, M.S., G. Dresselhaus, and P.C. Eklund. 1995. Science of Fullerenes and Carbon Nanotubes. Academic Press. 1024 p.

Ebbesen, T.W. 1994. Carbon Nanotube. Annu. Rev. Matter. 24 : 235-264.

Eric, W.W., W.M. Benjamin, and D.B. Luke. 1996. Growth of Metal Carbide Nanotubes and Nanorods. Chem. Mater. 8: 2041-2046.

Schmahl, N.G., Barthel, J. and G.F. Eikerling. 1964. Thermal decomposition of NiO Z.Anorg.Allg.Chem. 332 : 230.

Sloan, J., J. Cook, and J.R. Heesom. 1997. The encapsulation and in situ rearrangement of SnO insite carbon nanotubes. J.Cryst.Grow**.** 173 : 81-87.

Received date : 8/07/01
Accepted date : 28/09/01