



Comparison of Supported and Unsupported Co/Pd Nano Particles Catalysts to Synthesize CNT

**Ghazaleh Allaedini
Siti Masrinda
Zahira Yaakob
Jaafar Sahari
Meor Zainal Talib**

Abstract

In this paper the Co/Pd bi metallic catalyst have been prepared by sol gel method, one of them without using support and the other one by using MgO support, the articles have been characterized through FTIR, XRD, SEM and it has been concluded that the bi metallic catalyst using the support will lead to production of CNT (Carbon Nano Tube) with the higher yield, while the unsupported catalyst jus leads to the production of CNF (Carbon Nano Fibers)

Keywords: Supported catalyst, Un-supported catalyst, Co/Pd bi metallic nano particles, Nano carbon tubes, Nano carbon fibers.

1. Introduction

The discovery of CNT was in 1991 [1] since their discovery by Ijima, the CNT and the other structures of Carbon has attracted many researches for their research topic. Carbon can have various structures such as Graphite, Diamond, Fullerenes, Carbon Nano Tubes in form of Single wall, Multi wall and double wall, Graphene and also Carbon Nano fibers. [2]

CNT has many superior properties such as mechanical, electronics, optoelectronic and chemical, and that's the reason it has attracted many researches in industry and as well as academic purposes. They have so many superior applications in electronics , sensors , hydrogen storage, mechanical and field emission ,[3] super capacitates, semi conductors [4] and so many other commercial and industrial application review recently by Volder et al [5] .CNT can be produced by Arc discharge, laser ablation, electrolysis, from bulk polymer, low temperature solid pyrolysis, vertical/horizontal furnace, CVD (Chemical Vapor Deposition), PECVD (Plasma Enhanced Chemical Vapor Deposition) [6] .In the present paper the experiments are carried out in a CVD method since this method is better from the aspects of product purity and its large scale production [7]

2. Methodology

In the literature there are so many reports of using metallic catalysts and Co and Pd have always been proven to be among active catalysts. Bethune et al used bi metallic catalysts with cobalt and they could grow SWCNTs and they concluded that cobalt plays an important role in formation of SWCNTs [8]. Rasesco et al also produced SWNTs by Co-Mo bi metallic catalysts. [9] We have used Co because

Fe, Co, Ni have high solubility of carbon in these metals at high temperature and also high diffusion rate [10] They also have stronger adhesion with growing CNT [9] In addition to transition metals, the metals of other groups such as Au, Ag, Pt, Pd have been used to produce the CNT efficiently and with high yields. [11] Therefore because of these reasons the combination of Co and Pd have been used as a bi metallic catalyst in this paper. In the case of the support the MgO has been used among other supports such as Al₂O₃, SiO₂, Zeolite etc, because it has been reported that MgO is easily dissolvable and easier to purify in CNT. [12]

3. Experiments

There are many reports on production of Co-Pd bi metallic catalysts [13, 14, 15, 16, 17]. In this experiment Co(NO₃)₃.9H₂O, Pd(Br)₂(MeCN)₂ which was heated were dissolved in distilled water, they were stirred while heating at 100 C, then they were sonicated for 1 hr, The metal contents was kept at 6 wt% and the molar ratio of co-pd was 1:2. They were dried at 100 C and calcined at 500 C. The Co-Pd catalysts then were impregnated at MgO with an aqueous solution. They were stirred followed by drying in oven at 100 C and Calcination at 600 C. The 200 mg of the catalysts were placed in a reactor, heated in Ar up to 50 C when purged and then up to 800 C and after the temperature was stabilized the methane was introduced with a flow rate of 100 cm³/m³ for 6 hrs.

4. Results and Discussion

As shown in Figure 1, the particle size were determined by XRD and by an analysis of line broadening at 2θ for the supported catalysts at 25,43,68, 75 and for the unsupported catalysts at 2θ= 26, 36,43, 53, 67. It is found that the smaller uniform and more uniform Carbon Nano tubes have been grown from the MgO supported catalysts in contrast to the supported catalysts the un-supported ones have a broader diameter and the Fibers are grown in different structures and only few of these fibers are regular in shape.

The SEM result of the supported Co-Pd catalyst shows that multi wall carbon nano tubes are presence and the size distribution is homogenous however for unsupported the structure is Carbon Nano Fibers and Graphite like shape and there exists a different size distribution.

The FTIR results also show that when the support isn't used the band shifts and it's as if there is a mono metallic catalyst such as Co and the band for Pd almost has disappeared. On the activity of the catalyst, this fact can be mentioned that Co-Pd/MgO catalysts are more assisting in growing of CNT; however the Co-Pd unsupported catalyst has a very small yield producing CNF. This fact shows the carbon deposition rate which the support increases and consequently the steady state rate which increases the yield but the unsupported catalyst is not assisting the deposition rate and it deactivates the catalyst finally.

Figure-1. SEM result of (a) Co/Pd supported on MgO and (b) Co/Pd unsupported Catalyst

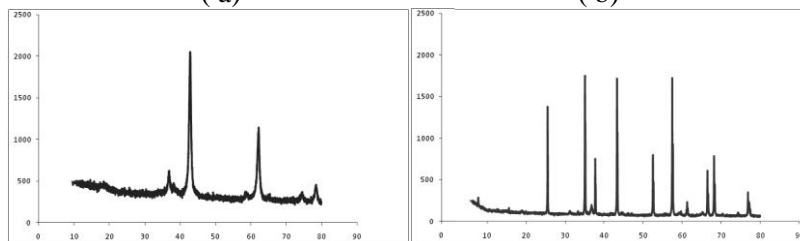


Figure-2. FTIR result of (a) Co/Pd supported on MgO and (b) Co/Pd unsupported Catalyst

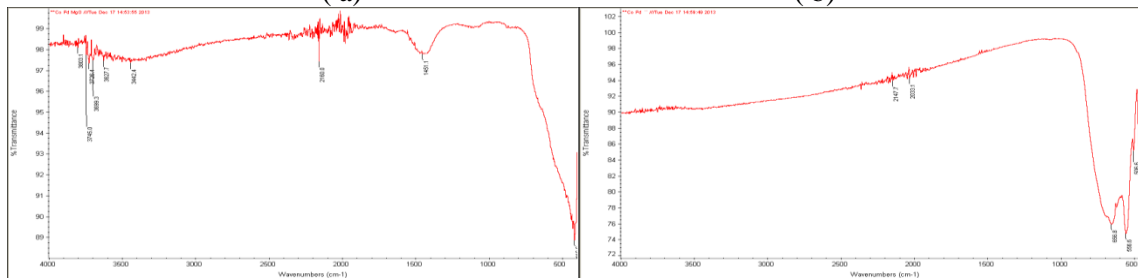
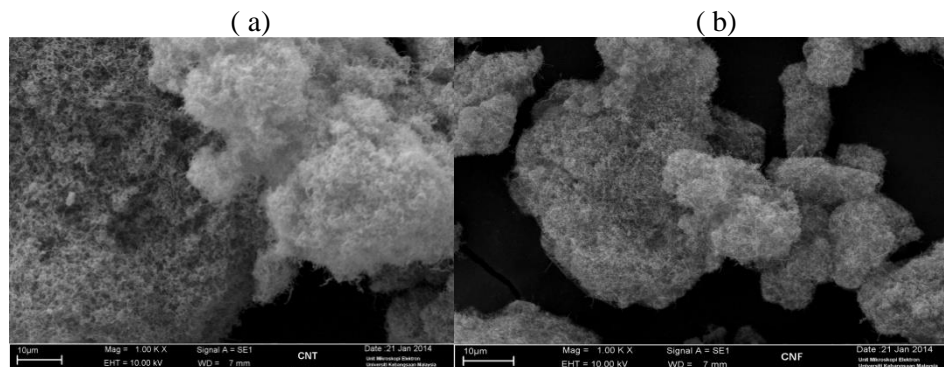


Figure-3. SEM result of (a) Co/Pd MgO supported resulted in CNT and (b) Co/Pd unsupported resulted in CNF



5. Conclusion

Generally the unsupported Co-Pd was inactive. This unsupported bi metallic catalyst just acted as mono metallic catalyst which was inactive without support and produced CNF which wasn't homogenous in shape and structure. The CNF on an unsupported catalysts are heterogeneous in diameter and size and the yield is so low. The bi metallic supported Co-Pd catalyst supported on MgO leads to the higher yield of CNT with a desired shape and structure and these facts are in accordance with the other researches done on the comparison of using support and unsupported catalyst in synthesis of CNTs. [18-27]

References

- [1] S. Iijima, *Nature*, 354: 56. (1991).
- [2] C. Liu, Y. Y. Fan, M. Liu, H. T. Cong, H. M. Cheng, M. S. Dresselhaus, *Science*, 286(1127): 404-405. (1999).
- [3] Pulickel, M., Ajayan¹ and Otto, Z., Zhou², M. S., Dresselhaus, G., Dresselhaus, Ph. Avouris (Eds.): *Carbon nanotubes. Topics Appl. Phys.*, 80: 391–425 (2001) *Applications of Carbon Nanotubes*
- [4] Z. Wu, et al., *Transparent, conductive carbon nanotube films. Science*, 305: 1273 (2004).
- [5] Michael, F. L., De Volder, Sameh, H., Tawfick, Ray, H., Baughman, A. John Hart *Carbon Nanotubes: Present and future commercial applications. Science*, 339. (2013).
- [6] B. Bhushan, *Springer handbook of carbon nano tubes, introduction to nanotechnology. 3rd Edn.*, pp: 62-68. (2010).
- [7] Manyamas, S., Kojima, R., Myanchi, Y., Chiashi, S. and Kohno, M., *Low temperature synthesis of high purity SWCNTs from alcohol. Chem. Phys let*, 360: 229. (2002).
- [8] D. S. Bethune, C. H. Kiang, M. S. De Vries, G. Gorman, R. Savoy, J. Vazquez and R. Beyers, *Cobalt-catalysed growth of carbon nanotubes with single-atomic-layer walls. Nature*, 363: 605-607. (1993).

- [9] Irurzun, Veronica. M, Yongqiang, Tan. and Daniel, E., Resasco, Sol-Gel synthesis and characterization of Co-Mo/Silica catalysts for single-walled carbon nanotube production. *Chem. Mater.*, 21: 2238–2246. (2009).
- [10] Kumar, M. & Ando, Y., (2010). Chemical vapor deposition of carbon nanotubes: A review on growth mechanism and mass production. *Journal of Nanoscience and Nanotechnology*, 10: 3739-3758.
- [11] Ding, F., Bolton, K. and Rosen, A., (2004). *J. Chem. Phys. B*, 108: 17369-17377
- [12] Hue, P., Wang, Liu. Y., Wang, B., Zhu, D., Synthesis of SWNTs using MgO. *Synthesis Metal*, 135-136: 833. (2003).
- [13] Heemeier, M., Anders, F., Carlsson, Naschitzki, M., Schmal, M., Bäumer, M., H.M.Freund preparation and characterization of a model bimetallic catalyst: Co–Pd nanoparticles supported on Al₂O₃. *Angewandte Chemie International Edition*, 41(21):4073 - 4076. (2002).
- [14] Ramírez, L, Serrano, R.M, Pineda, T., Román, F., Raptis, R and Cabrera, R, ,Synthesis and characterization of palladium and palladium–cobalt nanoparticles on vulcan XC-72R for the oxygen reduction reaction, *ACS Appl. Mater. Interfaces*, 5(22): 11603–11612. (2013).
- [15] Carlsson, A.F., Naschitzki, M., Baumer, M. and H.-J. Freund, The structure and reactivity of Al₂O₃ supported cobalt palladium particles: A CO-TPD, STM, and XPS Study *J. Phys. Chem. B*, 107: 778-785. (2003).
- [16] Lee, K.P., Se-Hee, Lee., Sundaram, K.S., Iyengar, G.A., Preparation of Co/Pd alloy particles dispersed multiwalled carbon nanotube supported nanocatalysts via gamma irradiation. *Radiation Physics and Chemistry*, (012; 81(9):1422–1425.
- [17] Ershov, B.G., Anan'ev.A.V, Abkhalimov, E.V., Kochubei, DI., Kriventsov, V.V., Yu. Molina.L.M, N. Yu. Kozitsyna, S. E. Nefedov, M. N. Vargaftik, I. I. Moiseev , Bimetallic Pd-M (M = Co, Ni, Zn, Ag) Nanoparticles containing transition metals: Synthesis, characterization, and catalytic performance *Nanotechnologies in Russia*, 6(5-6): 323-329. (2011).
- [18] Toebes, M.L., Blitter, J.H., Van Dillen, A.J., De Jong, K.P., Impact of the structure and reactivity of nickel particles on the catalytic growth of carbon nanofibers. *Catalyst Today*, 76: 33-42. (2002).
- [19] M.S. Kim, N.M. Rodriguez, R.T.K. Baker, *J. Catal.*, 131: 60. (1991).
- [20] N.M. Rodriguez, M.S. Kim, R.T.K. Baker, *J. Catal.*, 144: 93. (1993).
- [21] A. Chambers, N.M. Rodriguez, R.T.K. Baker, *J. Mater. Res.*, 11: 430. (1996).
- [22] N. Krishnankutty, N.M. Rodriguez, R.T.K. Baker, *J. Catal.*, 158: 217. (1996).
- [23] Park.C, N.M. Rodriguez, R.T.K. Baker, *J. Catal.*, 169: 212. (1997).
- [24] Park.C, R.T.K. Baker, *J. Catal.*, 179: 361. (1998).
- [25] Park.C, R.T.K. Baker, *J. Catal.*, 190: 104. (2000).
- [26] Anderson.P.E, N.M. Rodriguez, *J. Mater. Res.*, 14: 2912. (1999).
- [27] Park.C, M.A. Keane, *Langmuir*, 17: 83-86. (2001).
- [28] Mildred S. Dresselhaus, A.J, Mario H.G Dresselhaus and Saito.R, Perspectives on Carbon Nanotubes and Graphene Raman Spectroscopy 10.1021/nl904286r | *Nano Lett.* XXXX, xxx