Production of Multi-walled Carbon Nanotubes via Catalytic Decomposition of Methane in the Chemical Vapor Decomposition process

GHAZALEH ALLAEDINI[1*], SITI MASRINDA TASIRIN[1], PAYAM AMINAYI[2], ZAHIRA YAAKOB[1], MEOR ZAINAL MEOR TALIB[1]

[1]Department of Chemical and Process Engineering, University of Kebangsaan Malaysia, UKM Bangi, Selangor, Malaysia

[2] Chemical and Paper Engineering, Western Michigan University, Kalamazoo, Michigan, USA

[*]Corresponding author email: jiny_ghazaleh@yahoo.com,masrinda@eng.ukm.my , phone: +603-89218428

Abstract: In this paper, carbon nanotubes (CNTs) were synthesized via vapor deposition of methane as a carbon source in the presence of Ni/MgO catalyst. The catalyst crystallinity and morphology was examined by XRD and SEM and its superior size distribution and crystallinity was confirmed. The catalytic methane decomposition was conducted in a chemical vapor deposition reactor at 900 °C. Methane, with the flow rate of 600 ml/min, was used as a carbonous gas and hydrogen and nitrogen were used at the flow rate of 500 ml/min. The obtained carbon was characterized by transmission electron microscopy (TEM) and recognized to be multi-walled carbon nanotubes with an average diameter of ~8.6 nm. The Raman spectrum confirmed a high graphitization degree of the obtained CNTs with an I_D/I_G ratio of 2.05, indicative of high crystallinity with few structural defects. Moreover, the thermal analysis showed the high oxidation stability of the multi-walled carbon nanotubes. It was concluded that Ni/MgO catalyst can be used as an active catalyst in the production of multi-walled carbon nanotubes (MWCNTs) in the vapor phase deposition process.

Keywords: Ni/MgO catalyst, methane decomposition, multi-walled carbon nanotubes.

I . INTRODUCTION

Multi-walled carbon nanotubes (MWCNT) were discovered by Iijima in 1991[1]. Later in 1993, single-walled carbon nanotubes (SWCNT) were discovered by the same researcher[2]. Carbon nanotubes with form of Bamboo shaped has been reported as well.[3] Since the discovery, research about the different methods of production, properties and applications of carbon nanotubes has been continued. Although all carbon nano structures, including fullerenes, graphene and nanotubes are of great interest, CNTs have many unique physical and electrical properties [4] which make them an ideal candidate for numerous applications from field emission sources[5] to anti-cancer agent[6].

There are a number of methods to produce carbon nanotubes, including arc discharge, chemical vapor deposition, plasma enhanced chemical vapor deposition, laser ablation, and high-pressure CO conversion production[7] and CO2 conversion [8]. However, chemical vapor deposition (CVD) is still the most dominant method of high-volume carbon nano structures production [9] which typically utilizes a fluidized bed reactor that enables a uniform gas diffusion and heat transfer to the metallic catalyst nanoparticles employed in the CNT production[10]. In a CVD process, CNTs are produced via the decomposition of a gaseous carbon-containing hydrocarbon source at an elevated temperature in the presence of a transition metal catalyst [11]. A high nanotubes production yield can be achieved using this method. In addition, the product obtained using this approach tends to posses high purity and the growth of the carbon nanotubes requires a lower temperature in the range of 550-1000 °C when compared to other methods. This renders the process cheap, easy for lab scale production, and suitable form as production for commercial applications[12]. Finally, when catalyst is supported with a substrate, the growth of nanotubes can be controlled in a desired direction with respect to the substrate[13, 14].

As mentioned earlier common transition metals such as Ni, Co, Fe have been used in the production of carbon nanotubes. Despite the fact that MgO has been shown to be a superior support in the production of carbon nanotubes [15], there are no comprehensive reports which examines the utilization of such materials in the production of carbon nanotubes via chemical vapor deposition of methane gas. In this work MgO supported nickel was used as a novel catalyst in the production of

carbon nanotubes. Additionally, the prepared CNTs were examined in order to identify the potentials of MgO as a support material in the carbon nanotube synthesis.

II. METHODOLOGY

Magnesium Oxide (MgO), M=40.3 g/mol was purchased from R&M chemicals, Malaysia. Hydrochloric acid (HCl), 37 wt% was purchased from Fisher Chemicals. Nickel (II) nitrate hexahydrate Ni $(NO_3)_2$, 99.99% trace metal basis and oleic acid 99% CH_3 $(CH_2)_7CH=CH(CH_2)_7COOH$ were purchased from Sigma Aldrich, U.S.

The employed catalyst synthesis process was a modification of a study by Budiredla et al. [16]. To synthesize Mg-doped NiO nano particle catalyst, magnesium nitrate hexahydrate (Mg $(NO_3)_2 6H_2O$), nickel nitrate hexahydrate (Ni $(NO_3)_2 6H_2O$), and Oleic Acid ($C_{18}H_34O_2$) were used as precursors with ethanol as a solvent. 20 g of magnesium nitrate hexahydrate was added slowly to 100 ml of ethyl alcohol and stirred at 100 °C until the complete dissolution. Similarly, 10g of nickel nitrate hexahydrate was dissolved in 100 mL of ethyl alcohol. The obtained solutions were then mixed and oleic acid was added slowly to the obtained mixture at a constant stirring to produce a thick white gel. The product was dried at 100 °C for 24 hr to achieve Ni-doped magnesium. The result was then calcined for 4 hr at 600 °C.

For the CNT production, 5 g of the obtained catalysts were placed in the CVD reactor and heated in the presence of N_2 to 600 °C for 1 hr. The CVD reactor was then purged with H_2 and maintained for 2 hr at 600 °C. The temperature of the reactor was then increased to 1000 °C in the presence of N_2. Once the temperature was stabilized at 1000 °C, the methane gas was introduced to the reactor with a flow rate of 600 ml/min for 3 hr. The reactor was then cooled to ambient temperature while passing N_2 gas for 30 minutes. The schematic representation of the CVD process is shown in Figure 1. The obtained powder was collected and purified using 50 ml concentrated HCl for further characterization. XRD analysis was performed in a Bruker D8 Focus advanced powder diffractometer with a Cu Kα radiation of wavelength 0.15406 nm. Field emission scanning electron microscopy (FESEM) (Zeiss SUPRA55) micrographs were obtained to visualize the prepared catalyst as well as CNTs and determine their surface morphology at an operating voltage of 3 kV. Raman spectrophotometer with a laser of 532.230 nm wavelength (WITec, Model: Alpha 300R) was used to confirm the formation of

CNTs. Transmission electron microscopy (TEM) (Hitachi477700m) at an operating voltage of 10 Kv to investigate the nanotubes' diameter. Thermo gravimetric analysis (TGA) was performed (Metller Toledo Model: TGA/DSC1) at the resolution of 10 °C per 5 min to examine the CNTs' thermal properties.
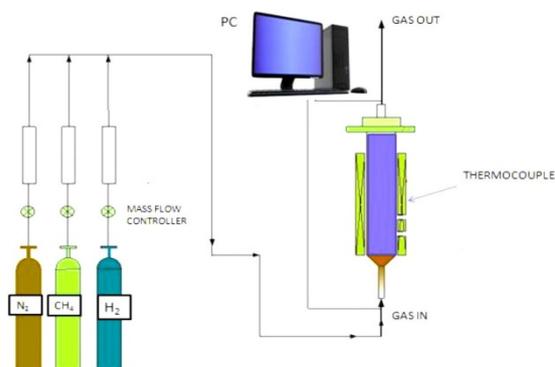

Figure1- Schematic representation of the CVD process for the production of carbon nanotubes

III. RESULT AND DISCUSSION

The SEM images of Ni/MgO catalyst are shown in Figure 2. Large surface area of the catalyst particles can be observed in this figure. As can be noted in the SEM micrographs, Ni-MgO particles, served as the catalyst and support for the CNTs production, exhibits flower/star like morphology.
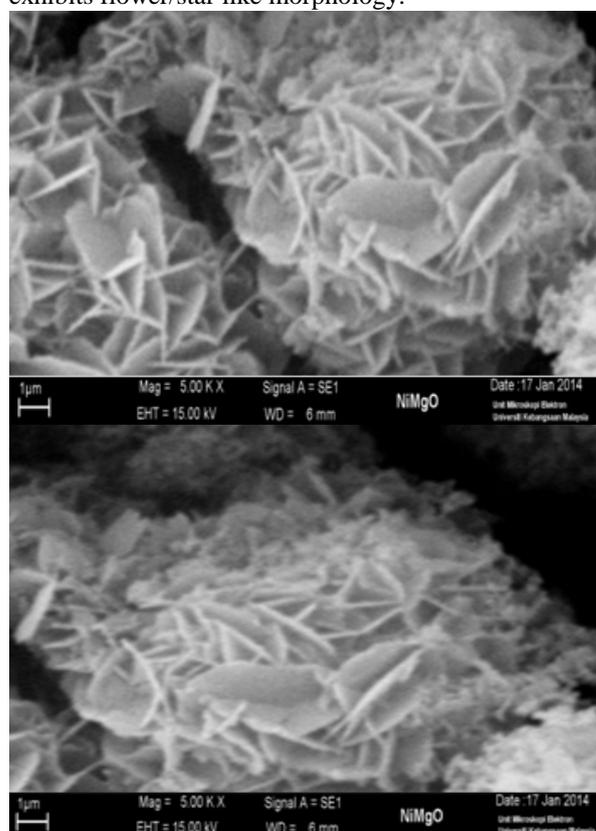
Figure 2-SEM micrographs of the flower-like Ni/MgO catalyst

XRD diffraction pattern of the Ni/MgO catalysts is presented in Figure3. XRD analysis was carried out to examine the crystalline structure of the catalyst. The peaks at $2\theta= 26°$, $38°$, $52°$, $58°$, and $68°$ are assigned to the planes of (111),(200),(220),(311), and (322) of Ni/MgO respectively. The volume-averaged crystalline size was calculated using Debye-Scherer's formula:

$$D = K\lambda/\beta\cos\theta, \qquad (1)$$

Where D is the crystalline size (nm), K is the Scherer constant equal to 0.89, λ is the radiation wavelength (nm), β is the observed peak width, and θ is the diffraction angle. The average particle size was calculated to be 32nm.
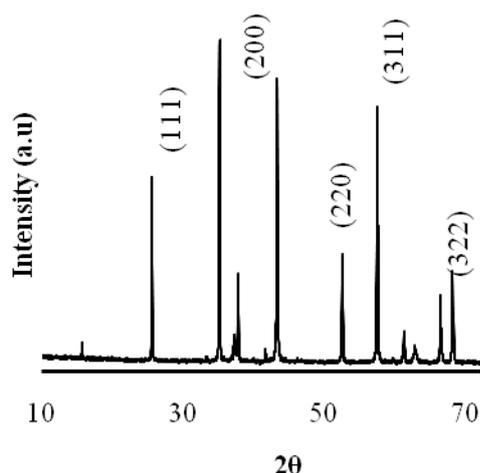
Figure 3-XRD diffraction pattern of the Ni/MgO catalyst with the calculated average particle size of 32 nm

The SEM micrographs of the grown carbon nanotubes are shown in Figure 4. The tubes grown amid the Ni/MgO flower-like catalysts are shown by arrows in Figure 4 (a). Carbon has been grown over the surface of the catalyst, suggesting that the catalytic methane decomposition has followed the tip growth mechanism to produce CNTs. Figure 4 (b) shows the high quality SEM images of the carbon nanotubes after the purification.
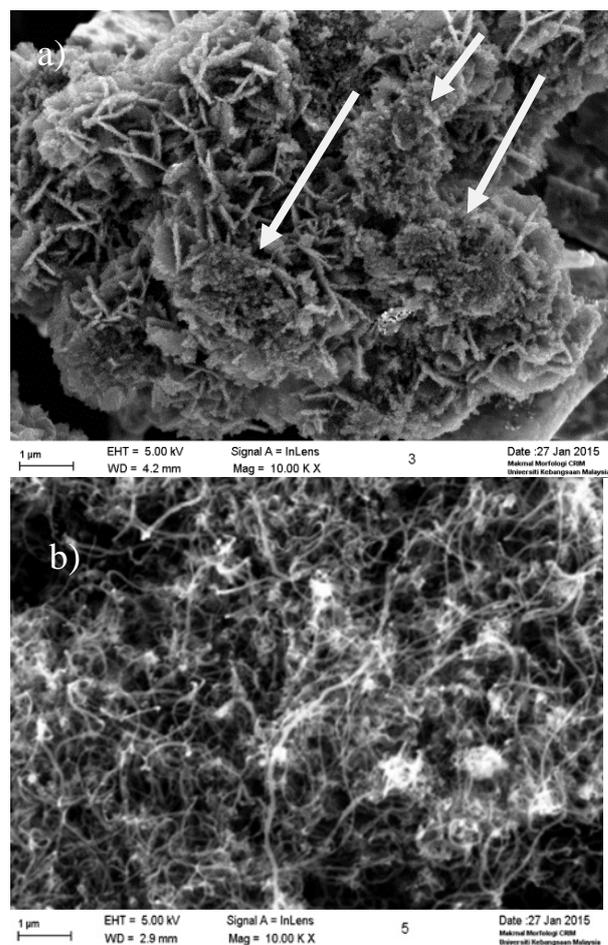

Figure 4-(a) SEM images of the grown carbon nanotubes in the presence of the prepared catalyst and (b) carbon nanotubes after the purification

Figure 5 shows the TEM images of multi-walled carbon nanotubes with an average diameter of 8.6 nm.
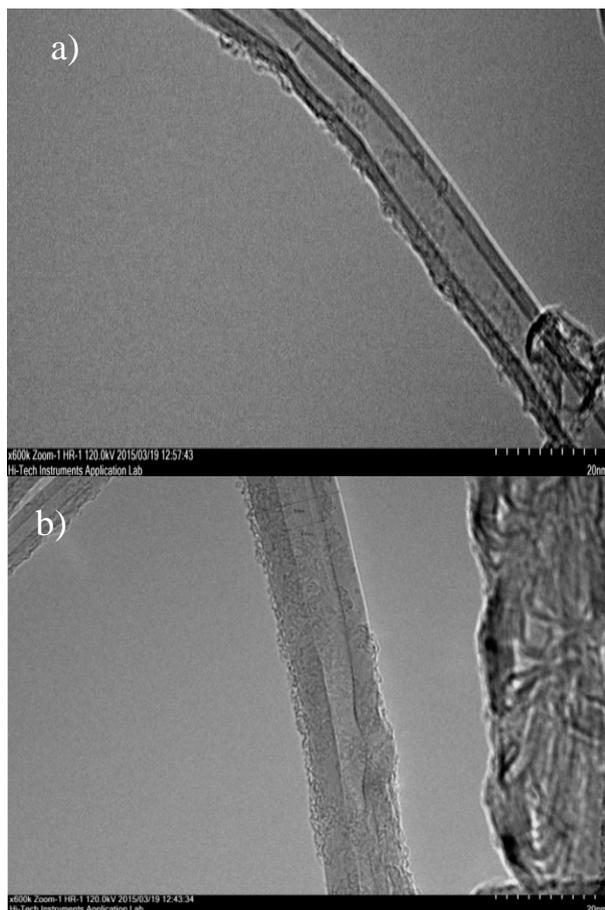
Figure 5- TEM image of a multi-walled carbon nanotube with an average diameter of 8.6 nm
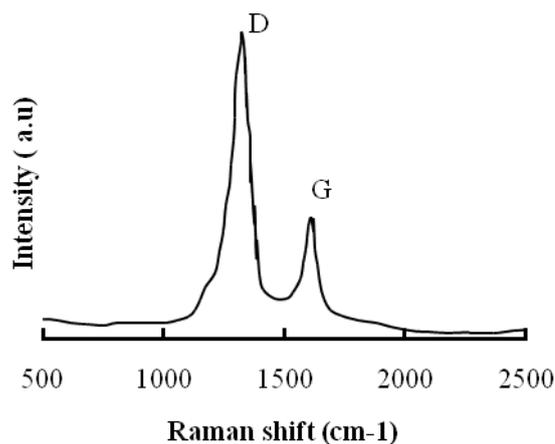

Figure 6-Raman spectrum of the obtained carbon nanotubes grown on the surface of the Ni/MgO catalyst, showing the I_D/I_G ratio of 2.05

Figure 7 shows the TGA curve of the obtained nano carbons. This figure shows the amount of weight loss as a function of temperature. Oxidative temperatures are reported to be around 330°C for amorphous carbon, and 500-700°C for MWCNTs, respectively [22, 23].As is observed in Figure 7, no weight loss was noted for the temperatures below 550°C. However, about 80 % weight loss is noted in temperatures between 550 and 700°C for the obtained CNTs which confirm the formation of MWCNTs.
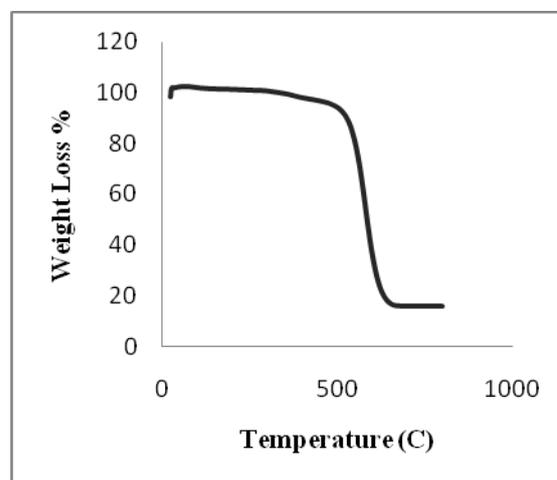

Figure 7-TGA curve of the obtained CNTs. ~ 80 % weight loss between 550 and 700 °C confirms the formation of MWCNTs.

Figure 6 shows the Raman spectrum of purified CNTs. Graphite-like carbon materials exhibit a Raman band at around 1580 cm^{-1} assigned to the G band, and a peak at 1350 cm^{-1} assigned to the D band. The D-band is known to depend on the disorder features of the hexagonal graphitic layers as well as the presence of small crystalline grains [17-19]. Since the G band is attributed to the tangential stretching mode of the graphite C=C bond, which is assigned to the vibration of sp^2-bonded carbon atoms in a two-dimensional hexagonal lattice, we can justly conclude the formation of graphitic nanotubes. The intensity of the D-band is inversely proportional to the effective crystallite size (L_a) in the direction of the graphite plane:

$$\frac{I_D}{I_G} = C \frac{\lambda_L}{L_a} \quad (2)$$

where I_D and I_G are the integrated intensities of the D and G bands, respectively, and C (λ_L) is the wavelength dependent pre-factor with the value of 4.36[20]. The I_D/I_G ration is an indication of the level of defects. The average value of I_D/I_G is determined to be 2.05 which is indicative of an satisfactory graphitization degree[21].

VI .CONCLUSION

Ni/MgO catalyst was prepared, characterized and employed for the production of carbon nanotubes in a vapor deposition reaction. Multi-walled carbon nanotubes were synthesized successfully by the

decomposition of methane over the surface of the prepared catalyst. TEM micrographs confirmed the formation of the multi-walled carbon nanotubes with the diameter of 8.6 nm. Raman spectroscopy results suggested a low degree of defects for the obtained CNTs. Moreover, high oxidation stability was observed from the TGA results. It can be concluded that Ni/MgO can be successfully used in the production of carbon nanotubes.

References:

[1] S. Iijima, "Helical microtubules of graphitic carbon," *nature,* vol. 354, pp. 56-58, 1991.

[2] S. Iijima and T. Ichihashi, "Single-shell carbon nanotubes of 1-nm diameter," 1993.

[3] G. Allaedini, S. M. Tasirin, P. Aminayi, Z. Yaakob, and M. Z. M. Talib, "Bulk production of bamboo-shaped multi-walled carbon nanotubes via catalytic decomposition of methane over tri-metallic Ni–Co–Fe catalyst," *Reaction Kinetics, Mechanisms and Catalysis,* pp. 1-12.

[4] H. Dai, "Carbon nanotubes: synthesis, integration, and properties," *Accounts of chemical research,* vol. 35, pp. 1035-1044, 2002.

[5] J.-M. Bonard, N. Weiss, H. Kind, T. Stöckli, L. s. Forró, K. Kern*, et al.*, "Tuning the field emission properties of patterned carbon nanotube films," *Advanced materials,* vol. 13, pp. 184-188, 2001.

[6] H. Tahermansouri and F. Chitgar, "Synthesis of Isatin Derivative on the Short Multiwalled Carbon Nanotubes and Their Effect on the MKN-45 and SW742 Cancer Cells," *Journal of Chemistry,* vol. 2013, p. 7, 2013.

[7] E. T. Thostenson, Z. Ren, and T.-W. Chou, "Advances in the science and technology of carbon nanotubes and their composites: a review," *Composites science and technology,* vol. 61, pp. 1899-1912, 2001.

[8] G. Allaedini, S. M. Tasirin, and P. Aminayi, "Synthesis of CNTs via Chemical Vapor Deposition of Carbon Dioxide as a Carbon Source in the Presence of NiMgO," *Journal of Alloys and Compounds,* 2015.

[9] G. Allaedini, P. Aminayi, S. M. Tasirin, and E. Mahmoudi, "Chemical Vapor Deposition of Methane In The Presence of Cu/Si Nanoparticles as a Facile Method for Graphene Production," *Fullerenes, Nanotubes and Carbon Nanostructures,* pp. 00-00, 2015.

[10] M. F. De Volder, S. H. Tawfick, R. H. Baughman, and A. J. Hart, "Carbon nanotubes: present and future commercial applications," *Science,* vol. 339, pp. 535-539, 2013.

[11] M. Endo, T. Hayashi, Y. A. Kim, M. Terrones, and M. S. Dresselhaus, "Applications of carbon nanotubes in the twenty–first century," *Philosophical Transactions of the Royal Society of London. Series A: Mathematical, Physical and Engineering Sciences,* vol. 362, pp. 2223-2238, 2004.

[12] Q. Liu and Y. Fang, "New technique of synthesizing single-walled carbon nanotubes from ethanol using fluidized-bed over Fe–Mo/MgO catalyst," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy,* vol. 64, pp. 296-300, 2006.

[13] K. Koziol, B. O. Boskovic, and N. Yahya, "Synthesis of Carbon Nanostructures by CVD Method," in *Carbon and Oxide Nanostructures*, ed: Springer, 2011, pp. 23-49.

[14] G. Allaedini, P. Aminayi, and S. M. Tasirin, "The Effect of Alumina and Magnesia Supported Germanium Nanoparticles on the Growth of Carbon Nanotubes in the Chemical Vapor Deposition Method," *Journal of Nanomaterials,* vol. 501, p. 961231, 2015.

[15] E. D. Dikio, A. J. Kupeta, and F. T. Thema, "A Comparative Study of the Effect of MgO and CaCO3 as Support Materials in the Synthesis of Carbon Nanotubes with Fe/Co as Catalyst," *Journal of Chemistry,* vol. 2014, p. 6, 2014.

[16] N. Budiredla, A. Kumar, S. Thota, and J. Kumar, "Synthesis and Optical Characterization of Mg1-xNixO Nanostructures," *ISRN Nanomaterials,* vol. 2012, p. 8, 2012.

[17] F. Tuinstra and J. L. Koenig, "Raman spectrum of graphite," *The Journal of Chemical Physics,* vol. 53, pp. 1126-1130, 1970.

[18]   J. Robertson, "Amorphous carbon," *Advances in Physics,* vol. 35, pp. 317-374, 1986.

[19]   W. M. Silva, H. Ribeiro, L. M. Seara, H. D. Calado, A. S. Ferlauto, R. M. Paniago*, et al.*, "Surface properties of oxidized and aminated multi-walled carbon nanotubes," *Journal of the Brazilian Chemical Society,* vol. 23, pp. 1078-1086, 2012.

[20]   M. Matthews, M. Pimenta, G. Dresselhaus, M. Dresselhaus, and M. Endo, "Origin of dispersive effects of the Raman D band in carbon materials," *Physical Review B,* vol. 59, p. R6585, 1999.

[21]   S. K. Pal and R. P. Institute, *Growth of Carbon Nanotubes on Metallic Substrates and Study of Their Interfacial Transport Properties*: Rensselaer Polytechnic Institute, 2007.

[22]   B. Kitiyanan, W. Alvarez, J. Harwell, and D. Resasco, "Controlled production of single-wall carbon nanotubes by catalytic decomposition of CO on bimetallic Co–Mo catalysts," *Chemical Physics Letters,* vol. 317, pp. 497-503, 2000.

[23]   S. Tang, Z. Zhong, Z. Xiong, L. Sun, L. Liu, J. Lin*, et al.*, "Controlled growth of single-walled carbon nanotubes by catalytic decomposition of CH< sub> 4</sub> over Mo/Co/MgO catalysts," *Chemical Physics Letters,* vol. 350, pp. 19-26, 2001.