



Synthesis of carbon nanotubes using carbon dioxide (CO₂) as a carbon source via catalytic chemical vapour deposition (CCVD): A Short Review

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ABSTRACT

The present literature overviews the up-to date studies on the successful synthesis of carbon nanotubes using carbon dioxide (CO₂) as a carbon stock by catalytic chemical vapour deposition (CCVD); a low temperature and an ambient pressure technique. As would be discussed later, the success of this process depends on the type of catalyst/support used. Although the reaction parameters and mechanism need to be studied closely, the present review is paramount based on the trend and current status of the CCVD in harnessing carbon nanotubes using carbon dioxide feed stock.

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INTRODUCTION

Carbon dioxide (CO₂) is a significant greenhouse gas. Combustion from; oil, natural gas, and coal, soil erosion, deforestation, and animal agriculture continually increase the concentration of anthropogenic carbon dioxide in atmosphere which leads to global warming (Solomon, 2007). Unfortunately, carbon dioxide being one of the more abundant and economical gas (Simate, Iyuke, Ndlovu, Yah, & Walubita, 2010) is rarely used in industrial processes (Freund & Roberts, 1996). The limited use and lack of interest in CO₂ chemistry can be explained by its thermodynamic stability (low energy content) and high kinetic barrier of its molecule (Freund & Roberts, 1996; Mackay, Shiu, & Ma, 1997). Carbon dioxide (CO₂) is thermodynamically made active if hydrogen is employed as co-reactant and stable compound is formed by exploiting the second oxygen in CO₂. Furthermore, the interaction of metal complex with CO₂ by thermal splitting (Rayne, 2008) in homogenous reaction or with solid/biological surfaces in heterogeneous reaction would free the kinetic barrier (Freund & Roberts, 1996).

However, the impetus as per utilisation and surface science study start with the pivotal role played by CO₂ in the methanol synthesis in the early 1980s (Freund & Roberts, 1996). Since then various industrial processes have been exploiting the CO₂

importantly to address the environmental issues of global warming.

Carbon nanotubes (CNTs) are cylindrical structures made of carbon atoms, possessing diameter of nanometer order but length of micrometers. Owing to their exceptional thermal conductivity, mechanical, and electrical properties, carbon nanotubes find applications in almost all the walks of life: media, transport, health, environment, entertainment and communication (Kumar & Ando, 2010).

CNTs can be synthesised by arc-discharge, laser-ablation, and chemical vapour deposition (CVD) or catalytic chemical vapour deposition (CCVD), (Danafar, Fakhru'l-Razi, Salleh, & Biak, 2009; Shifrina, 2011; Szabó et al., 2010). CVD/CCVD is the most popular, simplest, economical, low temperature, ambient pressure, more pure and high yield, most easy to scale-up, offers better structural control or CNT architecture, enables more harnessing plenty of hydrocarbons feed stock in any state (solid, liquid or gas), allows numerous use of substrates, offers better control on the growth parameters and enables CNT growth in many forms, namely powder, thin or thick films, aligned or entangled, straight or coiled nanotubes on predefined sites of a patterned substrate than either of arc-discharge or laser-ablation (Kumar & Ando, 2010).



The present literature would review the synthesis of carbon nanotubes by CVD/CCVD using CO₂ as carbon precursor. It starts with an overview on the CNT synthesis by other techniques, then reports the successful experiments where CNTs were synthesised by CVD/CCVD method emphasising on the role of reaction parameters that influenced the production of CNTs.

OVERVIEW OF THE CNT SYNTHESIS BY NON-CVD/CCVD TECHNIQUES USING CO₂

The CNTs have been synthesised by reduction of CO₂ in supercritical state [$>31^{\circ}\text{C}$, $>73\text{ atm}$] with various metals/metal based compounds (Chen & Lou, 2009; Lou, Chen, Chen, & Gao, 2005; Lou, Chen, Wang, & Zhang, 2003; Motiei, Rosenfeld Hacoheh, Calderon-Moreno, & Gedanken, 2001). Although the processes involved low temperature and are catalyst free, the high pressure above critical point would be problematic when the method is employed for commercial purposes.

Other methods used to synthesise CNTs and carbon nanofibers (CNFs) are electrolytic conversion of atmospheric CO₂ dissolve in molten salts and carbonates respectively (Novoselova et al., 2008; Ren, Li, Lau, González-Urbina, & Licht, 2015).

Synthesis of CNTs from CO₂ by CVD/CCVD

To the best of my knowledge, only three successful experiments were reported in the literature; in two of which fixed beds CCVD were used and the other explored floating CCVD reactor.

Xu & Hung (2007) reported to have successfully synthesised MCNTs using CO₂ by fixed bed CCVD over Fe/CaO catalyst/support (prepared by impregnation method) with crooked and branching morphology, diameter of around 50 nm, little structural defect, scalable, and total yield of over 50% relative to the weight of catalyst/support used. They identified the success behind their pressure-less (atmospheric pressure) technique to the concentration of catalyst/support, the support CaO, and reaction temperature (CNTs were produced in temperature range 790°C - 810°C). At 790°C straight and crooked MCNTs were observed from the TEM micrographs, as temperature increases to 810°C only branch CNTs were seen. When Al₂O₃, SiO₂, and MgO

were used as support, CNT was not produced. Also, they explained the growth mechanism to have involved the decomposition of carbon precursor into carbon atom, dissolution of these atoms in the catalyst metal particles, saturation, and precipitation of the tubular carbon deposit (vapour-liquid-solid [VLS] growth model). Although, a flow rate of 1:2 that is $750\text{ cm}^3\text{ min}^{-1}$ and $1500\text{ cm}^3\text{ min}^{-1}$ were used for the CO₂ and H₂ gases respectively, no any rational was given for the choice. Therefore, there is a need for a more comprehensive study/optimisation of the process parameters.

Allaedini, Tasirin, & Aminayi (2015) also reported a successful synthesis of CNTs via chemical vapour deposition (fixed bed) of carbon dioxide as a carbon source in the presence of Ni/MgO catalyst/support prepared by coreduction technique. They obtained purer, tube-like MCNTs structure, 8.45 nm average diameter, 27.38% yield of the total weight. The synthesis temperature range were 800°C - 1100°C , and the CO₂ and H₂ flow rate were $900\text{ cm}^3\text{ min}^{-1}$ and $1500\text{ cm}^3\text{ min}^{-1}$ respectively. The growth mechanism also proceeded by vapour-liquid-solid (VLS) growth model with claim that the CO₂ at 1000°C exist in supercritical state (calculated pressure 10 kbar); which facilitate a rapid decomposition of CO₂ to carbon nanotube with the assistance of MgO support. This claim demands for more realistic support and also the reaction parameters in this study need to be optimised.

In a research carried out by Simate *et al.* (2014) carbon nanotubes were produced from carbon dioxide in a Swirled floating catalytic chemical vapour deposition reactor (SFCCVD reactor) using Fe/CaCO₃ catalyst/support prepared by impregnation technique. They obtained MCNTs in the temperature range 750°C - 840°C with average diameter 100 nm. The crystallinity increases with temperature, suggesting smoother surfaces and less structural defects of the as-synthesised CNTs. Unlike the previous studies that used the vapour-liquid-solid (VLS) growth model, with the growth rate assumed to have depended on carbon diffusion over the catalyst nanoparticles, mass transfer in the gas phase, catalyst surface reactions, etc., they proposed that the growth rate may as well depends on gas phase decomposition reactions; specifically, the thermal decomposition of CO₂. With this



assumption, they were able to come up with the first kinetic model for the production of CNTs from CO₂. Using the model, they computed the quantity of CNTs at various concentration of CO₂. Also find out by these researchers were: experimentally measured fabrication rate fits the model at low concentration of CO₂; the developed model is useful to other carbon precursors; high concentration and flow rates of CO₂ adversely affect CNT growth rate; and no CNT production

at temperature below 750°C and above 840°C, and the optimum growth temperature is 800°C. Unlike the previous researches, the reaction parameters namely; carbon dioxide concentration, volumetric flow rate, and reaction temperature were studied, optimised, and compared with the result obtained from simulated model. Table 1 below, summaries the up-to date processes, findings and important reaction parameters for the reported research works.

Table 1: CNTs synthesis via CVD/CCVD using CO₂ as carbon precursor summary

Authors	Process	Result/Findings	Important reaction parameters
Xu and Huang (2007)	CCVD using Fe/CaO, CO ₂ , H ₂ &Ar gases; flow rate of CO ₂ &H ₂ are 750 cm ³ min ⁻¹ and 1500 cm ³ min ⁻¹ respectively	MCNTs; crooked & straight at 790°C, branched at 810°C, Ø≈50 nm, little defect, scalable, % yield relative to catalyst/support used > 50%	Temperature 790°C-810°C, catalyst support CaO, and Conc. Fe/CaO 1:10.
Simate et al (2014)	SFCCVD using Fe/CaCO ₃ , CO ₂ , H ₂ , &Ar	MCNTs; filamentous, av. Ø≈100 nm, little defect	Temperature 750°C-840°C, opt. temp≈800°C, low conc. & flow rate of CO ₂ , Fe/CaCO ₃ 1:10
Allaadini et al (2015)	CCVD using Ni/MgO, CO ₂ , H ₂ &Ar gases; flow rate of CO ₂ &H ₂ are 900 cm ³ min ⁻¹ and 1500 cm ³ min ⁻¹ respectively	MCNTs; tube-like, av. Ø≈8.45 nm, little defect, 27.38% of total weight of Ni/MgO (catalyst/support used)	Ni/MgO catalyst/support
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CONCLUSION

Based on this review, the synthesis of carbon nanotubes using one of the greenhouse gas (CO₂) via catalytic chemical vapour deposition could be promising and cater for mass production of CNT chiefly by more abundant carbon source, atmospheric pressure and low temperature process if the reaction parameters are studied and optimised.

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