

## The international debate on Effect of Cobalt Catalyst Confinement in Carbon Nanotubes Support on Fischer-Tropsch Synthesis Performance

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Pre-treating the multi-walled carbon nanotubes (CNTs) support by refluxing in 35 vol% nitric acid followed by heating at the temperature of 600 to 900 °C resulted in the formation of defects on the CNTs. Increasing the temperature of the pre-treatment of the CNTs from 600 °C to 900 °C, enhanced the fraction of cobalt-oxide nanoparticles encapsulated in the channels of CNTs from 31% to 70%. The performance of Co/CNTs in Fischer-Tropsch synthesis (FTS) was evaluated in a fixed-bed micro-reactor at a temperature of 240 °C and a pressure of 2.0 MPa. The highest CO conversion obtained over Co/CNTs.A.900 was 59% and it dropped by ~3% after 130 h of time-on-stream. However, maximum CO conversion using Co/CNTs.A.600 catalysts was 28% and it decreased rapidly by about 54% after 130 h of time-on-stream. These findings show that the combined acid and thermal pre-treatment of CNTs support at 900 °C has improved the stability and activity of the Co/CNTs catalyst in FTS.

Recent developments on the applications of Co-based catalyst on carbon materials support in Fischer-Tropsch synthesis (FTS) have been reviewed by Mark E Dry where a new option and challenges in catalysis for the Fischer-Tropsch Synthesis (FTS) have been highlighted. Carbon support exhibits weak interaction with the cobalt and the resultant microstructures greatly influenced the activity and stability of the Co-based catalyst in FTS. Santiago et al. reported metastable carbides nanoparticles are active catalysts and the electronic structure of metal significantly affects catalytic activity. Metals such as Ni, Co or Fe with few d-vacancies can synthesize metastable carbides that are desired catalysts to nucleate and grow CNTs. The unique physical characteristics of carbon nanotubes, such as mechanical, electrical, porosity, and thermal conductivity as well as its unique chemical properties rendered them

a suitable option as a catalyst support. Due to the inertness of the CNTs and its weak interaction with metals, surface modification of CNTs has to be performed. Nitric acid is typically used to functionalize the surface of CNTs and it has been established that the CNT surface become more reactive upon oxidation. Storsæter et al. reported that under optimum oxidation conditions, maximum surface area, pore size, defects and oxygen content can be achieved. CNT support with the highest degree of functionalization stabilized Co nanoparticles and resulted in high performance FTS catalyst. Davis and co-workers reported that oxidation in air up to 400 °C produced defects, however upon annealing in vacuum at a much higher temperature (1800 °C), the CNTs became more ordered compared to 'as received- CNTs'. Tavasoli et al. discovered that thermal treatments of CNTs following the acid refluxing step effectively removed the oxygen-containing functional groups (such as  $-C=O$ ,  $-COOH$ ,  $-OH$ ) on the external surface of CNTs, resulting in controllable encapsulation of Co particles inside the channels of CNTs. They applied a wetness impregnation method (without pH control) to deposit Co on the treated CNTs and found that CNTs pre-treated at 650 °C resulted in 80% of cobalt nanoparticles deposited inside the channel of the CNTs and that it exhibited the highest activity and selectivity to C5+ hydrocarbons in FTS.

In this study, we used the same approach of combined acid and thermal pre-treatments of CNTs as that of Tavasoli et al. but we applied the strong electrostatic adsorption (SEA) method to prepare the Co/CNTs catalyst where the pH of the precursor solution was controlled during the metal deposition. Schwarz suggested that the electrostatic forces between a metallic ion and a charged support could be utilized for direct adsorption of the metallic ion over surfaces including two oxide fractions. The idea behind this

method has been efficiently applied to make highly dispersed, monometallic catalysts on a multitude of oxide and carbon supports. In a natural way hydroxyl (–OH) groups on the surface of an oxide become protonated or deprotonated when the contacting solution pH is acidic or basic, respectively. These charged hydroxyl groups are then in a position to uptake metal complex ions in a solution of opposing charge. The density of the charged hydroxyl groups on the oxide surface depends on its Point of Zero Charge (PZC), i.e., the pH at which the surface is neutrally charged. Above the PZC, the hydroxyl groups become deprotonated and render the surface negatively charged and cationic complex can be adsorbed onto the surface via strong electrostatic adsorption method.

Previous studies conducted on the CNTs-supported cobalt catalysts utilized the impregnation method without pH control during the preparation of the catalyst. In this work, the deposition of cobalt on the pre-treated CNTs support was performed at selected pH, based on the SEA principle. The pH of the precursor cobalt solution was controlled during the synthesis step. The effects of combined acid and thermal pre-treatments of CNTs support on the properties and performance of Co/CNTs catalysts are discussed. We have established that the combined acid and thermal pre-treatments of CNTs at 900 °C improved the activity and stability of the Co/CNTs catalyst in FTS.

Carbon nanotubes were supplied by Nanostructures & Amorphous Materials Inc., Los Alamos, NM, USA (purity > 95%, chemical vapor deposition (CVD), length: 10–20 µm, diameter: 30–50 nm) and functionalized via refluxing with 35 vol% nitric acid (Merck) for 15 h at 110 °C. The mixture was filtered and washed with deionized water until the pH reached 7. Acid-treated CNTs were then thermally treated at 600 and 900 °C in flowing argon at 20 mL min<sup>-1</sup> for 3 h. This thermal pre-treatment was performed to reduce the oxygen containing groups on the external surface of the CNTs, as previously reported. Samples with acid and thermal pre-treatments at different temperatures were designated as follows: CNTs. A, CNTs.A.600 and CNTs.A.900. The last 3 digits in the sample coding represent the temperature (°C)

at which thermal pre-treatment was conducted on the acid-treated CNTs. The purity of the CNTs did not change significantly after the pre-treatment steps.

Strong electrostatic adsorption (SEA) method was used as the catalyst preparation method for the Co/CNTs sample. Based on the principles of the SEA method, the surface of functionalized CNTs would become negatively charged when the pH of the contacting solution was higher than the point of zero charge (PZC) of the CNTs. The PZC of the CNTs used in this work was found to be 9.5. Based on previous studies [16], the maximum cobalt uptake on the CNTs occurred when the cobalt precursor solution was kept at pH of 14. Therefore, the adsorption of cobalt ions on the pre-treated CNTs was performed at pH 14 using an aqueous solution of Co(NO<sub>3</sub>)<sub>2</sub>. The samples were then filtered and air dried for 24 h. Dried samples were calcined in a tubular furnace at 400 °C for 4 h under Ar flow. The metal loading on CNTs was kept at 10 wt. % during the preparation stage. The actual amount of Co in the Co/CNTs sample was found to be 9.5 wt. % via AAS measurements.

#### Catalyst Characterization

For determination of textural properties, samples were degassed at 200 °C for 4 h under 50 mTorr vacuum and were analyzed by N<sub>2</sub>-adsorption (Micromeritics, ASAP 2020, (Norcross, GA, USA)). The reduction trend of the catalysts was analyzed by using a Thermo Finnigan TPD/R/O 1100 at Universiti Teknologi PETRONAS (UTP) prepared with a thermal conductivity detector and a mass spectrometer. Typically, 30 mg catalyst was located the U-shaped quartz pipe. Catalyst were degassed under a nitrogen gas at 200 °C to eliminate traces of moisture and gases from catalyst pores and then cooled to ambient temperatures. TPR was carried on using 5% H<sub>2</sub>/N<sub>2</sub> with a rate of 20 mL min<sup>-1</sup> and heating from 40 to 800 °C at 10 °C min<sup>-1</sup>. The TPD results was used to find out and analyze cobalt dispersion. For TPD tests, 30 mg of calcined samples was reduced under hydrogen gas at 370 °C for 6 h and then cooled to 40 °C.

**Biography:**

Dr. Omid Akbarzadeh is working with Nanotechnology and Catalysis Research Centre since 2016. His main research area is heterogeneous catalysis and catalytic reaction engineering. He has spent 10 years in academic-industrial projects as a research officer and post-doctoral. Dr. Omid has worked 5 years in the oil and gas industry as a chemical engineer. He developed advanced smart catalysts especially for oil and gas industries. Dr. Omid has contributed to two PETRONAS Research Sdn Bhd industrial catalyst projects and worked on international Airbus R&D project in NANOCAT. Currently, he is the PI of graphene catalyst project in Hokkaido University in Japan, project member of FRGS grant in UTP and assigned to the NANOCAT center project. Dr. Omid was the Chairman, keynote speaker and organizing committee of many international conferences. He is currently supervisor of three Ph.D. students from different countries. He has published many ISI papers; book chap-

ters and has two approved and granted patents. Also, he has hands-on experience and passed several pieces of training on handling different types of equipment which are being widely used for material synthesis, characterization and performance evaluation. He is in close collaboration with other departments, government agencies and universities around the world. He is visiting researcher of Jiangsu University China and Hokkaido University Japan. He is member of the society of petroleum engineers (SPE) and Senior Member of Hong Kong Chemical, Biological & Environmental Engineering Society. Omid awarded full fellowship from UTP during Ph.D and were involved for lab demonstrator and teaching in the different courses of chemical engineering. He awarded Silver Medal in 27th International Invention & Innovation Exhibition (ITEX 2016), Kuala Lumpur Convention Center in Malaysia and Silver Medal of Post Graduate Research Project in 35th Science & Engineering Design Exhibition (SEDEX 35).