

## ABSTRACT

In this study the synthesis and use of carbon nanofibers (CNFs) as catalysts supports for Fischer Tropsch synthesis is reported. The synthesis of carbon nanofibers with two distinct morphologies was optimized based on the reports in the literature that the straight (SCNF) and helical (CCNF) carbon nanofibers grow on Cu catalysts with different particle sizes. To selectively grow CNFs with a single morphology Cu catalysts were designed using different synthesis procedures (by using unsupported, coated and silica supported catalysts). The prepared copper oxide (CuO) nanoparticles were characterized by techniques such as TEM, XRD and nitrous oxide chemisorption. These techniques showed that the unsupported and coated CuO catalyst precursors has large particle sizes (range 100-300 nm) and thus had low Cu atomic surface area, while the supported CuO catalysts displayed low particles sizes in the nanoscale regime (<20 nm) and hence had high atomic surface area. Preparation of CNFs was carried out 300 °C using acetylene (C<sub>2</sub>H<sub>2</sub>) gas as the carbon source. Cu catalysts with large particle sizes resulted in straight CNFs and the small supported Cu nanoparticles grew helical CNFs because of the change in the nanoparticle surface energy during adsorption of the acetylene gas and the silica (SiO<sub>2</sub>) support effects that limited Cu nanoparticles from sintering (i.e. final particles size ~ 60 nm). Soxhlet extraction proved to be an invaluable step in removing adsorbed polycyclic aromatic hydrocarbons.

Because of the low thermal stability of these CNFs the materials were then annealed at higher temperatures ranging from 500-1400°C in an inert environment (passing N<sub>2</sub> gas). The helical CNFs snapped under high temperature annealing ( $\geq 900$  °C) resulting in shorter lengths in comparison to the straight CNFs. BET analysis of the annealed CNFs indicated that the CNFs annealed at 500 and 900 °C have increased surface area and have a mesoporous pore structure with the surface area ranging from 200-350 m<sup>2</sup>/g. Raman and Fourier transform IR spectroscopy indicated that the CNFs annealed at 500 and 900 °C, (which were the main material of interest because of their high surface area and thermal stability) had different hybridized carbon content. CNFs annealed at 500 °C contained both sp<sup>2</sup> and sp<sup>3</sup> hybridized carbon while annealing the CNFs at 900 °C resulted in a complete rehybridization of the carbon content to sp<sup>2</sup>. The carbon sp<sup>3</sup> content in the CNFs annealed at 500 °C therefore implied that CNFs annealed at this temperature are more defective in comparison to the CNFs annealed at 900 °C. Since it is well known that material functionalities are affected by the

amount of defects present inside the different CNFs were then applied as catalyst supports for Fischer Tropsch synthesis (FTS) to compare the support effects on cobalt active sites.

The CNF surfaces were first modified by functionalization using concentrated  $\text{HNO}_3$  solution. The preparation of the catalyst systems was performed by a simple HDP method using urea. The CNFs and the FT catalysts were characterized using different techniques such as XRD, TEM, BET, TPR and Raman spectroscopy. Reactor studies performed at 220 °C ( $P = 8$  bar,  $\text{GHSV} = 1200 \text{ mL}\cdot\text{h}^{-1}\cdot\text{g}_{\text{cat}}^{-1}$ ) showed the catalysts had activities with CO conversion ranging from 25-45%. It was observed that catalysts supported on CNFs annealed at 500 °C displayed higher average activities of about  $\pm 15\%$  (based on the CO conversions) in relation to the catalysts supported on CNFs annealed at 900 °C. Catalysts showed minimal water gas shift reaction and high methane selectivity (i.e.  $\sim 20\text{-}30\%$ ) which can be attributed to the small Co crystallite sizes and low pressure reaction conditions.