

## O-Functionalized CNT Mediated CO Hydro-Deoxygenation and Chain Growth

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**Abstract :** Worldwide energy independence is reliant on the ability to leverage locally available resources for fuel production. Recently, syngas produced through gasification of carbonaceous materials provided a gateway to a host of processes for the production of various chemicals including transportation fuels. The basis of the production of gasoline and diesel-like fuels is the Fischer Tropsch Synthesis (FTS) process: A catalyzed chemical reaction that converts a mixture of carbon monoxide (CO) and hydrogen ( $H_2$ ) into long chain hydrocarbons. Until now, it has been argued that *only* transition metal catalysts (usually Co or Fe) are active toward the CO hydrogenation and subsequent chain growth in the presence of hydrogen. In this paper, we demonstrate that carbon nanotube (CNT) surfaces are also capable of hydro-deoxygenating CO and producing long chain hydrocarbons similar to that obtained through the FTS but with orders of magnitude higher conversion efficiencies than the present state-of-the-art FTS catalysts. We have used advanced experimental tools such as XPS and microscopy techniques to characterize CNTs and identify C-O functional groups as the active sites for the enhanced catalytic activity. Furthermore, we have conducted quantum Density Functional Theory (DFT) calculations to confirm that C-O groups (inherent on CNT surfaces) could indeed be catalytically active towards reduction of CO with  $H_2$ , and capable of sustaining chain growth. The DFT calculations have shown that the kinetically and thermodynamically feasible route for CO insertion and hydro-deoxygenation are different from that on transition metal catalysts. Experiments on a continuous flow tubular reactor with various nearly metal-free CNTs have been carried out and the products have been analyzed. CNTs functionalized by various methods were evaluated under different conditions. Reactor tests revealed that the hydrogen pretreatment reduced the activity of the catalysts to negligible levels. Without the pretreatment, the activity for CO conversion as found to be  $7 \mu\text{mol CO/g CNT/s}$ . The O-functionalized samples showed very activities greater than  $85 \mu\text{mol CO/g CNT/s}$  with nearly 100% conversion. Analyses show that CO hydro-deoxygenation occurred at the C-O/O-H functional groups. It was found that while the products were similar to FT products, differences in selectivities were observed which, in turn, was a result of a different catalytic mechanism. These findings now open a new paradigm for CNT-based hydrogenation catalysts and constitute a defining point for obtaining clean, earth abundant, alternative fuels through the use of efficient and renewable catalyst.

**Keywords :** CNT, CO Hydrodeoxygenation, DFT, liquid fuels, XPS, XTL

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