

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 (H₂) 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 H₂, 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 pre-treatment 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 hydro-deoxygenation, DFT, liquid fuels, XPS, XTL.

I. INTRODUCTION

MATERIALS [1] and processes capable of producing alternative energy technologies hold the key to our future energy security. Fischer Tropsch (FT) synthesis process [2], [3], a catalyzed chemical reaction, can convert mixture of CO and H₂ into clean burning fuels. FT fuels have significant benefits over other fuels (such as low particulate emission) and are compatible with modern automobile engines. Typical FT catalysts (cobalt and iron [4]-[7]), are prepared over oxide supports [8]-[10]. The support restricts the reduction of the catalyst to their metallic form, leading to less efficient FT process [11]-[14]. We have shown that as-grown CNTs can produce FT fuels with extremely high conversion efficiencies (at least two orders of magnitude) than the present state of the art FT catalysts. Tailored synthetic fuels with desired carbon chain lengths (containing 12-14 carbon atoms (jet fuel) or 14-20 carbon atoms (diesel)) were readily obtained by simple tuning of the reaction parameters (such as temperature) using the CNTs. Our findings demonstrate that CNTs represent an elite class of highly competent, robust, support free catalyst systems. Such enhanced catalytic activity not dependent on transition metal catalysts was intriguing. This paper presents the details of studies that answered the two fundamental questions that arose from our previous findings a) How does CO hydrogenation proceed on CNT surfaces, and b) How does carbon chain growth propagation proceed on CNT surfaces? Experimental reaction studies integrated with catalyst characterization and DFT calculations have helped elucidate the mechanism and activity of the CNT surfaces. It was identified that O functional groups were the key for CO adsorption, dissociative H₂ adsorption and subsequent chain growth with some key differences from the conventional carbene mechanism. Further studies to deliberately increase the O-functional groups have been conducted and are presented here.

II. EXPERIMENTAL PROCEDURES

A. MWNT Synthesis and O-Functionalization

Multiwalled aligned CNTs were produced by air assisted floating catalyst CVD method. Xylene was used as the source of the carbon and ferrocene was used as the catalyst. The as produced CNTs were then treated with HCl for one hour to

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remove majority/all of the Fe. The purified CNTs obtained was then washed several times to remove any HCl. These purified and washed CNTs were then treated with 35 % H₂O₂ or 70 % HNO₃ for adding the O functional groups. When treating with H₂O₂ the material was ultrasonicated for 30 min followed by stirring for 24 hrs. For the HNO₃ treatment, the mixture was ultrasonicated for 10 minutes and then refluxed for 6 hrs. The resulting solids were filtered washed and dried.

B. Material Characterization

The as-produced and treated CNTs were analyzed using TGA, electron microscopy, XPS and FTIR to identify the presence of the functional groups, the residual Fe as well as the morphology.

C. CO Hydro-Deoxygenation Experiments

Reactions with 1:1 syngas was performed in a ½ in dia X 18 in tube. The reaction zone temperature was maintained using a temperature controller and a heat tape. The pressure in the reaction zone was maintained with a back pressure regulator. The liquids were collected by cooling the exit stream. Further, the gases produced were analyzed on a MicroGC (every minute) while the liquids were analyzed using a GC/MS. The feed flow was controlled with Brooks Mass Flow Controller and the flow rates of the outlet gases were measured. The conversion, activity and selectivity were calculated based on the obtained data.

D. DFT

A detailed model of the reaction mechanism based on DFT calculations was developed for SWNT (6,6).

III. DATA ANALYSIS

Conversion is calculated by the number of moles converted as a percentage of the number of moles in the feed:

$$\text{Conversion} = \frac{N_{\text{CO, initial}} - N_{\text{CO, final}}}{N_{\text{CO, initial}}}$$

where the number of moles, N , is calculated using the real gas law $P_i V = NRT$. The partial pressure P_i is calculated using the measured value of pressure and the measured content of species i (in the case of conversion it is CO) obtained from the GC data. The activity is calculated by dividing the rate of the change in the mole of CO by the mass of the catalyst (CNTs).

IV. RESULTS AND DISCUSSION

A. Comparison of CO Deoxy-Hydrogenation Performance

The FT experiments were conducted with the as-produced CNTs with and without pretreatment in hydrogen. For the FT experiment, the syngas flow rate (H₂:CO =1) was kept at 15 mL/min and the reactor temperature and pressure were 350 °C and 300 psi, respectively. It was observed that the activity of the the CNTs after hydrogen treatment were negligible. However, the tests without hydrogen pretreatment showed an activity of greater than 7 μmol CO/g CNT/s. There are reports

of cobalt catalysts loaded onto CNTs that exhibited activities as high as 8.7 μmol CO/g Co/s and thus it is seen that the as-produced CNTs behave as strongly as Co. When the flow rate was increased to 80 mL/min, the activity values obtained were greater than 30 μmol CO/g CNT/s. Both the O-functionalized samples showed very activities greater than 85 μmol CO/g CNT/s (Fig. 1). However, it should be noted that this activity value was limited since the conversions (Fig. 2) were found to be near 100 % and thus it is expected that the actual activities are higher than reported here. It was generally observed that the activity evolved over time and then reached steady state. This is probably due to surface reconstruction leading to active sites. With this respect, it was found that the HNO₃ treated CNTs achieved the high activity values faster.

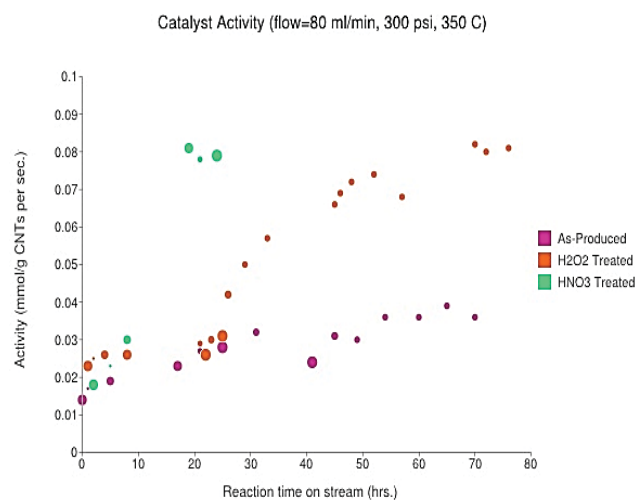


Fig. 1 Comparison of the activity of as-produced, HNO₃ and H₂O₂ treated MWNTs at a flow of 80 mL/min

Fig. 3 shows the differences in the liquid product distributions of the peroxide treated and the as-produced CNTs. The carbon chain length is clearly seen to shift towards the lower carbon numbers for the treated MWNT. In addition, the alkane to alkene ratio also increases for the treated sample.

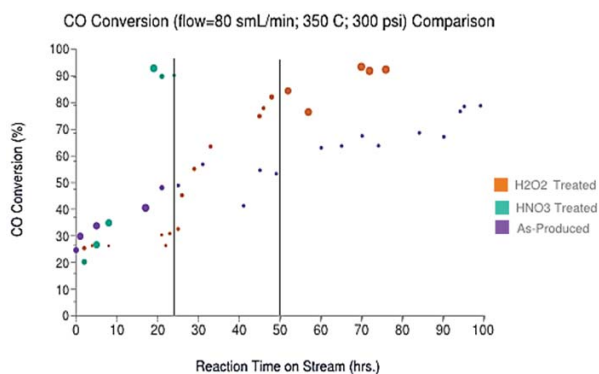


Fig. 2 CO Conversion for all three samples

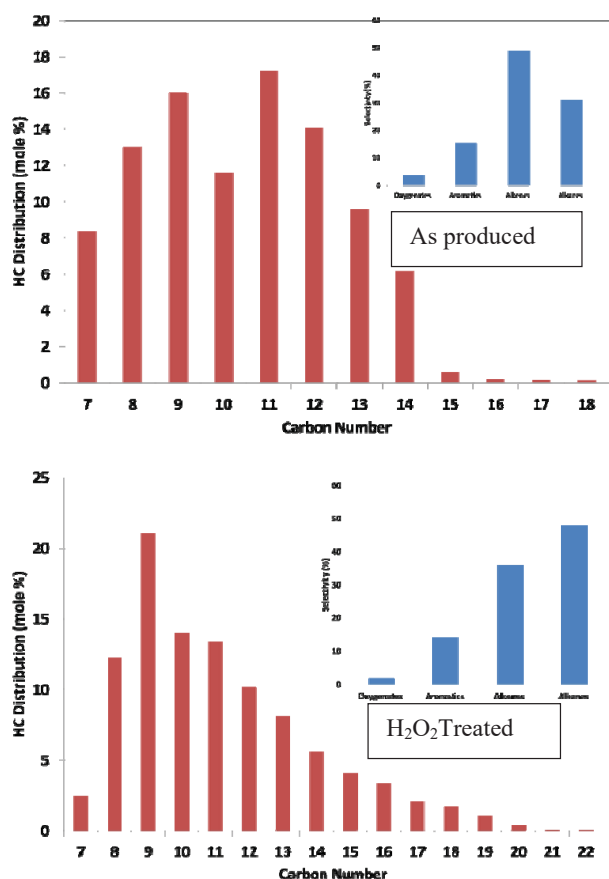


Fig. 3 Differences in Liquid Product Distribution

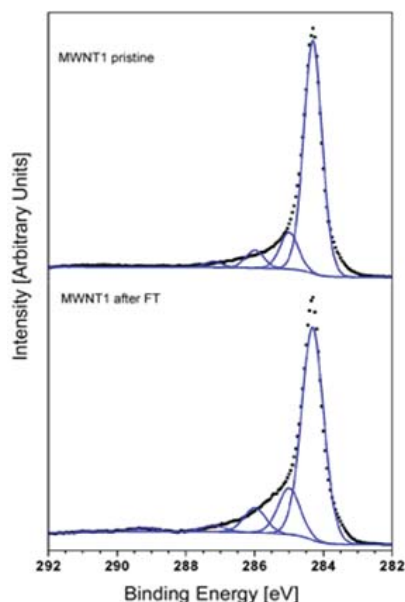


Fig. 4 C1s Line scan of catalyst before and after reaction

B. Catalyst Characterization and Correlation

The TGA data showed that the HNO₃ treated CNTs contained no residual Fe while the H₂O₂ treated samples

contained less than 0.5% residual Fe. It should be noted that the as-produced sample contained 3 % Fe. However the XPS data on all the samples did not show any presence of Fe which indicates that the Fe may be occluded and thus would not be able to participate in any reaction. XPS data further showed the oxygen groups such as C-O, O-H, COOH to increase due to the treatment. High resolution scan near the C1s region on the used CNTs clearly showed distinct presence of oxygen (bonded to carbon in various configurations). We also observed that the C-O and -COO peaks are broadened and increased in intensity for the sample obtained after FT experimentation as compared to the as-produced sample. The FT process (Fig. 4) seems to not only regenerate the groups identified as active sites for FT but actually increase the epoxy content on the surface. The peaks at ~284.3 eV were assigned to the C=C bonds of the hexagonal graphite lattice forming the surface of the CNTs (sp²). Features at ~286 eV were assigned to the C-O (carbon singly bound to oxygen as in phenols and ethers) attached to the CNT surfaces while those at ~287.5 were attributed to carbon doubly bound to oxygen as in ketones and quinones (C=O). Furthermore, the C1s spectra was deconvoluted to carbon bound to two oxygen atoms (-COO) as found in carboxyls, carboxyl anhydrides and esters. This explains the increase in activity as the reaction proceeds. The TEM images of the samples show that the acid treatment was not severe enough to open the tubes but had introduced some defects. In addition, the Fe found in the as-produced samples was not found in the TEM images of the acid treated samples.

C. Catalytic Mechanism

DFT calculations revealed that the C-O and OH functionalized CNT surfaces can adsorb CO and is kinetically and thermodynamically favored while it is not favored for pristine CNT surfaces. Calculations show that unlike the carbene mechanism, reactions on the functional groups on the CNTs proceed by a different route wherein the hydrogenation of the C atom of COOH and subsequent O cleavage. The authors claim that the hydrogenation of the C atom is not competitive. The formation of carbene occurs by the hydrogenation of the OH to form water and which is then followed by the hydrogenation of the newly created unsaturated C atom. The relatively close activation energies between the CO insertion and the long chain ending with COCOH may cause oxygenates, specifically alcohol to be more favored at higher temperature unlike FTS on transition metal catalysts which follow the carbene mechanism. This was confirmed in our experiments at 450 °C.

V. CONCLUSIONS

Experimental evidence of CO hydro-deoxygenation at the C-O / O-H functional groups on O-functionalized CNTs followed by subsequent chain growth was demonstrated. The data show that the reaction rates are dependent on the concentration of these functional groups on the CNT surfaces. DFT calculations performed to explain the observed phenomena are also discussed. It was found that while the

products were similar to FT products, the differences in selectivities were a result of a different mechanism. While the carbene mechanism is generally accepted for FT reactions on transition metal catalysts, it was found that CO insertion into the chain was more feasible. It was found that chain growth takes place without the O cleavage and with CO insertion. Further, it was evidenced that hydrogen treatment deactivated these catalysts while no deactivation was observed when treated with syngas with $\text{CO:H}_2 = 1$ for over 800 hrs..

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