

Nano-docking Stations for Synfuels Catalyst on Carbon Nanotubes

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ABSTRACT

Carbon Nanotubes (CNTs), based on their large surface area and many available adsorption sites, represent a distinctive class of catalyst supports for enhanced chemical reactions including fuel synthesis [1-4]. Unfortunately, the mobility of surface-bound catalytic nanoparticles (NPs) on CNTs typically results in agglomeration leading to a subsequent decrease in effectiveness of the catalytic activity over time [5,6]. In contrast, confinement of metal NPs inside the CNT channel has been demonstrated recently to significantly enhance catalytic activity and stability over time during ethanol production despite restricted accessibility factors of the nanotube's main channel [7]. Production of synfuels via Fischer-Tropsch process relies on nano-sized transition metal catalysts, predominantly iron or cobalt and we present a CNT system which limits the surface mobility of iron catalyst particles on CNT surfaces during fuel synthesis. The catalytic NPs in nanosized channels or "docking stations" are oriented normal to the CNT surface resulting in superior catalyst stability.

Keywords: Fischer-Tropsch, Synfuels, Carbon Nanotubes, Nano-catalysts, Sintering

1 INTRODUCTION

The Fischer-Tropsch Synthesis (FTS) process takes syngas, a mixture of carbon monoxide (CO) and hydrogen (H₂), and converts it into hydrocarbon fuels over transition metal catalysts [8,9]. Fuel synthesis via FTS is becoming increasingly important based on projected oil shortages, high crude oil prices, stringent environmental regulations and the fact that FTS can utilize synthesis gas produced from several sources including biomass which helps control CO₂ emissions [10,11]. Iron catalyst particles have been used for FTS either unsupported or supported including the use of CNT support surfaces [1,12-14]. Catalyst sintering, a process wherein the active metal nanoparticles agglomerate and lose effective surface area is a common mechanism of deactivation for FTS. Three dimensional surface structures on supports may offer new ways of protecting the catalyst against sintering by harboring the active catalyst nanoparticles such that surface movement is restricted by surface potential wells where the potential energy is minimized.

This research project addresses the need for advanced catalyst systems that have superior stability for synfuel synthesis. Carbon nanotubes (CNTs) were shown to provide not only excellent structural support for the FT catalyst but can uniquely host the catalyst particles inside nanosized docking stations that developed as a result of the nanotube /catalyst preparation method. Calcium is shown to play a significant role in the formation of the docking stations. The confinement or harboring of the Fischer-Tropsch-catalytic particles in the docking stations along the CNT walls is described for the first time and we believe that our discovery may apply to various other catalytic processes.

2 EXPERIMENTAL

2.1 Catalyst Preparation

CNTs were obtained through catalytic decomposition of C₂H₂ at 700 °C and 800 °C over Fe-supported on CaCO₃ (aragonite) as described elsewhere [15]. Purification of the CNTs was performed using 30-55 % HNO₃ solution. Catalysts with 5% and 10% Fe supported on CNTs and also mixed Fe-Co were prepared using incipient wetness (IW) impregnation process. Some samples were then further promoted with 0.25% Ru, K and Cu. All samples were dried (120 °C overnight) and calcined (heating in nitrogen at 220 °C for 2.5 hours) to decompose the salts.

The catalysts were tested in a fixed bed micro reactor after reduction in H₂ at 350 °C and 2 bars for 24 hours. At reaction temperature (275 °C) and pressure (8 bars), a flow of syngas (60% H₂, 30% CO, 10% Ar) was passed over all the catalyst with similar flow rate (space velocity 2142 h⁻¹).

2.2 Characterization Methods

Electron Microscopy studies were performed using a JEOL 2010F STEM outfitted with a URP pole piece, GATAN 2000 GIF, GATAN DigiScan II, Fischione HAADF STEM detector, and EsVision software. STEM images were acquired using either the high resolution probe at 2 angstrom or a 1nm analytic probe. STEM images were then deconvolved using the Lucy-Richardson algorithm. EELS mapping was performed using the 1nm probe, alpha of 10 mrad, and a beta of 2 mrad. Maps shown were derived from core edge intensity obtained after background

subtraction using an integration window ranging from 10 to 30 eV depending on the edge.

3 RESULTS AND DISCUSSION

Figure 1a shows the scanning transmission electron microscope (STEM) image of surface wells or docking stations that have been formed on a multi-walled CNT exterior surface. Each docking station consists of a 2-7 nm deep nanochannel with diameter varying from 2-4 nm. Figure 1b is a close-up view of 9 docking stations that harbor 1-2 nm sized catalyst NPs at the bottom and sides of each nanochannel. These docking stations can be seen in STEM mode by using a small mrad detection angle, which enhances the carbon signal at the edges of the CNT walls.

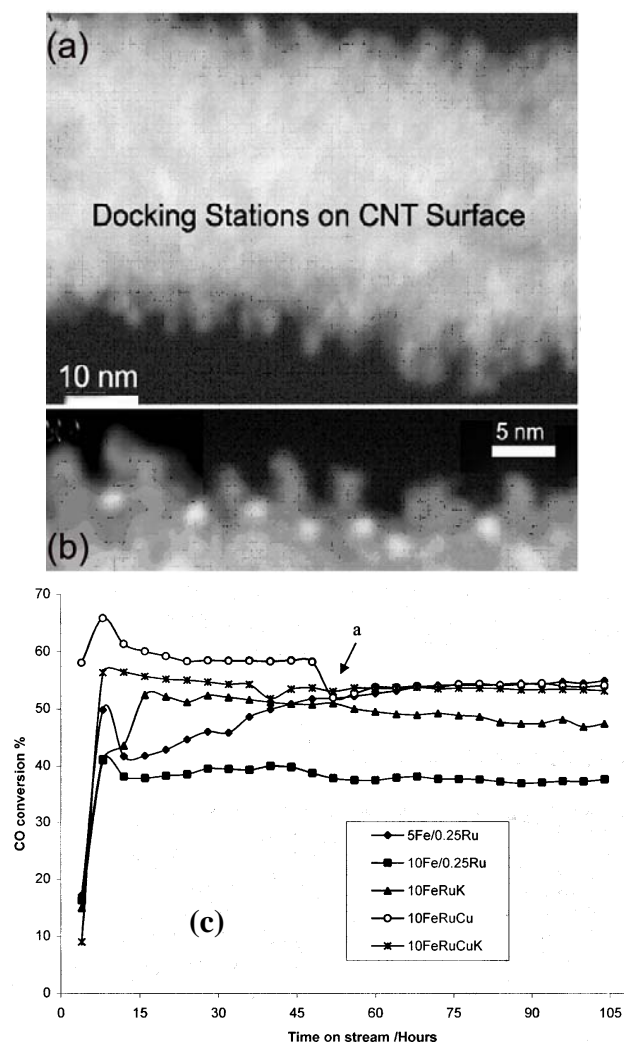


Figure 1 (a) HRSTEM image of carbon nanotube with nanosized docking stations along surface. (b) magnified view showing docking stations with Fe-NPs at the bottom or sides of the channels. (c) FTS using Fe-NPs supported on CNTs with docking stations has long-term stability for catalysts over 100 hours on stream.

Figure 1c shows the performance of the highly stable catalyst for the above described CNT-Fischer Tropsch catalyst system. The carbon monoxide (CO) conversion for a series of catalysts harbored in docking stations on CNTs showed no significant loss even after the catalysts spent over 100 hours on stream. Against this background the docking stations clearly play a dominant role in the increase of catalyst stability. Metal particle size plays an important role in FTS and other catalytic processes and sintering is undesirable. In general, metal NPs deposited on oxide or carbon tend to migrate and agglomerate on support surface to form bigger, less active particles during the catalytic process. The high degree of stability on stream during FTS (Figure 1c) with the current samples suggests that the catalyst did not deactivate or sinter appreciably. The 1-2 nm Fe particles are well dispersed and harbored in the nanochannels of the docking stations along CNT surface (Figure 1b) and the effective surface area of iron is much higher compared to unsupported or supported Fe catalysts where the particle size ranges from 5-100 nm.

CNT synthesis from acetylene utilized micron-scale calcium carbonate particles (aragonite; CaCO_3) as the structural support for catalysts in a temperature range of 700-800 °C. The as-synthesized CNTs were washed with HNO_3 , followed by incipient wetness impregnation of iron-precursor. Finally, a calcination step at 220 °C in nitrogen was performed. Despite of the acid wash calcium remains in the CNT system as shown in the dark field DF-STEM image in Figure 2a. A dense population of uniformly distributed 1-2 nm-sized Ca and Fe NPs were identified using electron energy loss spectroscopy (EELS) and the ultra-small particles decorate the CNT surface with Ca-NPs being more abundant compared with Fe-NPs. The image was obtained using a detection angle of 40 mrad using a Lucy-Richardson Deconvolution method (DeConvEELS is commercially available from HREM Research Inc (www.hremresearch.com)). It was determined through experimentation that this detection angle produced the best balance between the carbon and calcium dark field signals and noise level, producing the highest quality image of the Ca and Fe NPs. Here the docking station's dark field signal from the thin carbon on the CNT edges is greatly reduced by the larger detector scattering angle in order to make the Ca and Fe NPs clearly visible due to their larger atomic number, hence, larger scattering angle and, therefore, the docking stations are not visible in Figure 2a. Spatially resolved EELS at the nanoscale is well established and composition mapping was performed on the CNT surface to show the presence of Ca-NPs vs. Fe-NPs on the carbon support. EELS spectrum imaging was performed in order to determine the spatial relationship between the Ca and Fe-NPs on the CNT surface and results are shown in Figures 2c and 2d. This was accomplished using a JEOL 2010f STEM equipped with an ultra-high resolution pole piece, GATAN 2000 GIF, GATAN Digiscan 2, Fischione HAADF STEM detector and EMI spec, ES-Vision software. STEM images and EELS spectrum images were

acquired using the 1 nm analytical STEM probe. EELS acquisition utilized an alpha semi-angle of 20 mrad and a

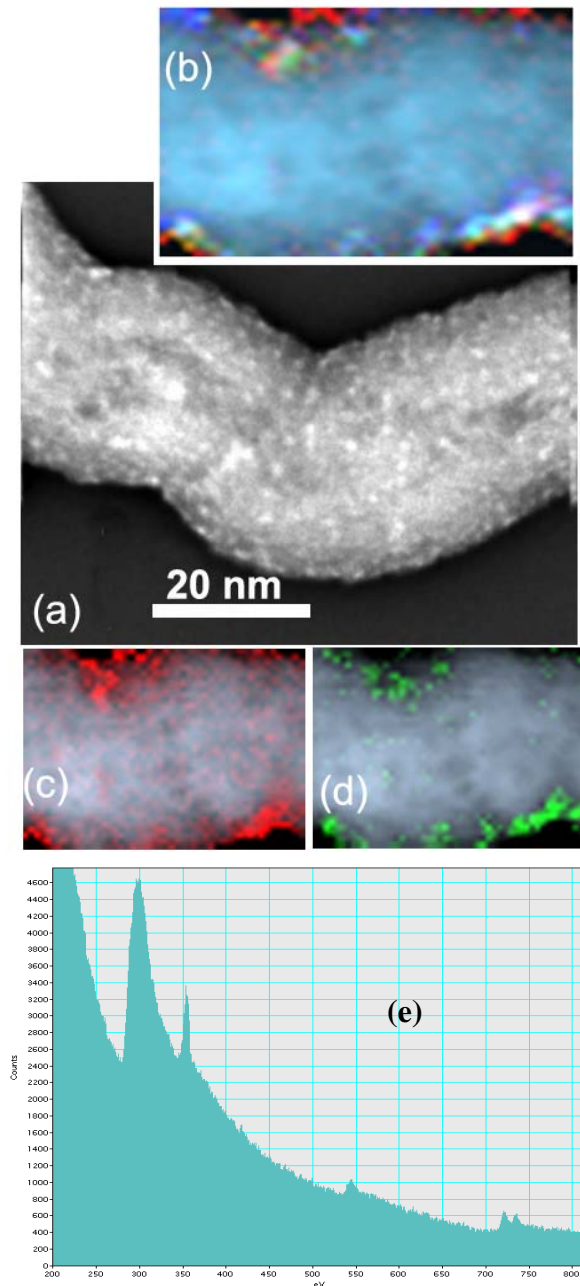


Figure 2 (a) DF-STEM image showing ultra-small (1-2 nm) Ca and Fe NPs dispersed on CNT surface. (b) EELS composition map illustrating Ca-NPs in green and Fe-NPs in red, oxygen in blue side-by-side. (c) and (d) Nanoscale EELS analysis of Fe and Ca with spatial distribution on CNT surface shown in (a); (e) EELS spectrum showing Carbon, Ca, O, and Fe.

beta semi-angle of 6 mrad. Maps shown in Figures 2c and 2d were derived from the core edge intensities obtained after background subtraction using an integration window ranging from 10-30 eV, depending on the edge. Relative color intensities in the display maps (Figure 2d, 2e)

qualitatively correlate to the absolute amounts of an element present. EELS-spectrum imaging was chosen over EDS mapping due to the superior sensitivity of EELS to light elements, particularly carbon and oxygen. This allows the use of a short dwell time of 0.1 seconds, which shortens mapping times considerably compared to the EDS mapping of light elements and minimizes the effects of sample instability and carbon deposition. Figure 2e is an EELS spectrum showing Carbon, Ca, O, and Fe observed in a particular docking station.

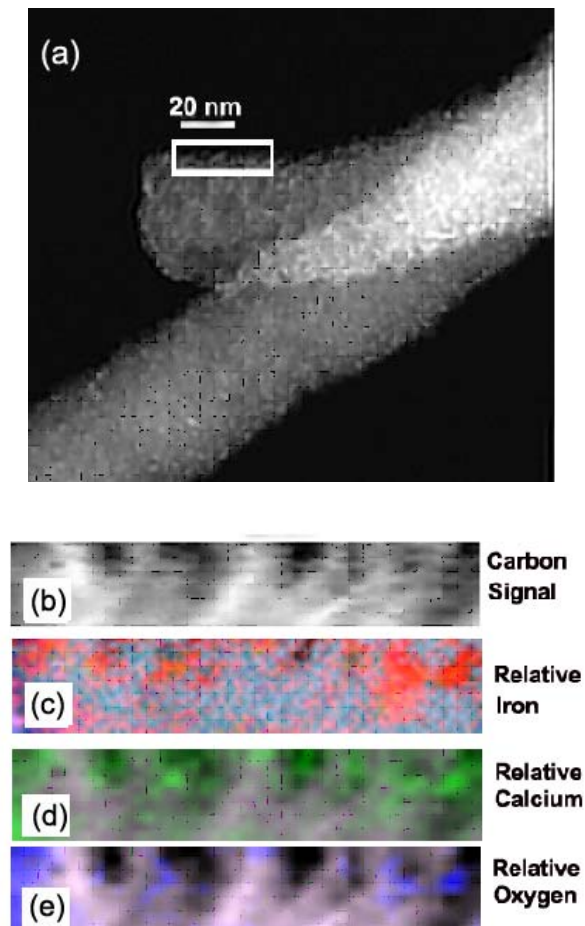


Figure 3 (a) shows HRSTEM of two CNTs with catalyst in docking stations. Insert at CNT exterior shows area where spatially resolved EELS was performed. (b) carbon signal shows presence of docking stations; (c) Fe-NPs inside docking stations; (d) Ca-NPs lining docking stations; (e) relative oxygen signal on CNT surface.

EELS spectrum imaging in Figure 3 clearly shows the spatial relationship between the Ca and Fe-NPs and the CNT docking stations. Analysis was done at the edge of a CNT (Figure 3a) and the carbon signal corresponds to the docking stations shown in Figure 3b while the presence of Ca and Fe inside the docking stations is shown in Figures 3b and 3c respectively. The relative oxygen signal is illustrated in Figure 3d. The presence of ultra small (~1

nm) Fe-NPs seems to always correlate with 1-2 nm Ca-NPs that are present on the contours of the CNT docking stations. EELS elemental maps described in Figure 3 clearly demonstrate the confinement of the ultra small Fe-FT catalyst particles within the docking stations of the CNTs along with abundant Ca-NPs. Some channels are seeded with Ca-NPs and lack Fe-NPs.

The event that led to the incorporation and confinement of Ca-NPs into the CNT walls was determined to occur during the calcination step of the catalyst particles rather than the CNT growth step itself as confirmed by STEM imaging and elemental analyses of CNTs during the various synthesis stages (CNT growth followed by acid washing, followed by iron precursor impregnation, followed by calcination at 220° C in nitrogen). Acid washing of the as-formed CNTs removed the bulk of aragonite support and only minor amounts remained on residual CNTs after acid wash. The high density of ultra-small Ca-NPs incorporated and confined in CNT surface layers as shown in Figure 2a and 3d could only be observed after calcination, suggesting that Ca may have led to disruption of CNT outer walls due to highly localized gasification along the CNT surface while the samples were treated at 220 °C under nitrogen. After calcination/local gasification step, STEM shows CNTs to have a highly-defined nanochannel structure where each surface channel is separated by a carbon ridge, leading to the observed alternating nanoscale “ridge and valley” morphology. In TEM mode the individual carbon ridges are distinguished as fullerenes (Figure 4) which occur on each side of a nanochannel or docking station. Some ridges are constructed of two or more vertically aligned fullerenes, which leads to deeper channels.

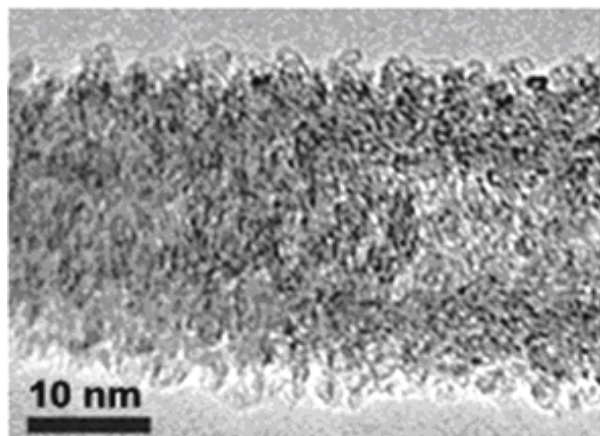


Figure 4 HRTEM illustrating CNT with fullerenes on surface. Fullerenes line nanochannels and connect to bend CNT walls

Disruption of outer walls and bending of the graphite planes may have led to the fullerenes observed in Figure 4a and increases local anisotropy of the CNT exterior which can result in an increase in active sites. The result is a highly advanced metal and/or metal oxide catalysts supported on carbon nanostructures and Fe-NPs are protected from

migration and coalescence on active carbon surface to maximize the effective surface area for FTS. Obviously, the 3D morphology of the CNTs plays a major role such that Fe-NPs are harbored in potential docking stations or surface wells where energy is minimized and restricts the catalyst particles from migrating out of these areas. The surrounding fullerene-ridges provide a natural activation energy barrier to Fe-NPs migration. The ultra-small particle size and high surface area of these Fe catalysts translates to high turnover frequency and higher yields for FTS process and their long-term stability, combined with high yields would lead to cost advantage for synthetic fuels derived from FTS process. Ongoing studies will reveal if Fe-catalyst particles inside the main CNT channel will lead to even greater stability compared with the current CNT-docking station system. Oxygen was also found to be localized along the outlines of the docking stations (Figure 3e) and may be important for oxidation catalysis with oxygen localized on defect sites on the carbon structures. On the other hand the presence of highly dense populated ultra-small Ca-NPs on the surface of CNTs is thought to provide novel scaffolds for synthetic bone growth and in general the docking stations may harbor useful promoters or catalysts for a variety of applications.

REFERENCES

- [1] G. Leendert Bezemer, Uwe Falke, A. Jos van Dillen et al., *Chem. Commun.*, **6**, 731 (2005).
- [2] M. K. van der Lee, A. Jos Van Dillen, J. H. Bitter et al., *J. Am. Chem. Soc.*, **127**, 13573 (2005).
- [3] L. Gucci, G. Stefler, O. Geszti et al., *J. Catal.*, **244**, 24 (2006).
- [4] X-H. Xia, Z-J. Jia, Ying Yu et al., *Carbon*, **45**, 717 (2007).
- [5] Y. Shao, G. Yin, Y. Gao et al., *J. Electrochem. Soc.*, **153**, A1093 (2006).
- [6] J. Solla-Gullon, E. Lafuente, A. Aldaz et al., *Electrochim. Acta*, **52**, 5582 (2007).
- [7] X. Pan, Z. Fan, W. Chen et al., *Nat. Mater.*, **6**, 507 (2007).
- [8] M. E. Dry and J. C. Hoogendoorn, *Cat. Rev. - Sci. Eng.*, **23**, 265 (1981).
- [9] B. H. Davis, *Fuel Process. Technol.*, **71**, 157 (2001).
- [10] M. Balat, *Energy, Education, Science and Tech.*, **17**, 83 (2006).
- [11] H. L. Chum and R. P. Overend, *Fuel Process. Technol.*, **71**, 187 (2001).
- [12] J. F. Schultz, M. Abelson, L. Shaw et al., *Journal of Industrial and Engineering Chemistry*, **49**, 2055 (1957).
- [13] M. Luo and B. H. Davis, *Appl. Catal., A*, **246**, 171 (2003).
- [14] M. C. Bahome, L. L. Jewell, K. Padayachy et al., *Appl. Catal., A*, **328**, 243 (2007).
- [15] M. L. Mabudafhasi, R. Bodkin, C. P. Nicolaides, X.-Y. Liu, M. J. Witcomb, N. J. Coville, *Carbon*, **40**, 2737 (2002).