

THE MORPHOLOGY OF FISCHER-TROPSCH-TYPE PRODUCTS. Joseph A. Nuth III¹ and Natasha M. Johnson², ¹Solar System Exploration Division, Code 690, NASA's Goddard Space Flight Center, Greenbelt MD 20771 USA (joseph.a.nuth@nasa.gov), ²Astrochemistry Branch, Code 691, NASA's Goddard Space Flight Center, Greenbelt MD 20771 USA.

Introduction: Fischer-Tropsch-type (FTT) reactions can occur at active catalytic sites on almost any grain surface [1,2]. We have previously demonstrated that the deposition of refractory carbonaceous material on the surfaces of such grains can actually enhance the rate of the FTT process [3]. We made a simple assumption that the carbonaceous coating grew to cover the surface of the underlying catalyst, leaving an outer coating that completely covered the original grain. Such "grain varnishes" or refractory organic residues have frequently been described in the past as the result of ultraviolet or radiation processing of ices containing simple organic precursors such as CH₄, CH₃OH, CH₂O and NH₃ [4, 5]. It seemed natural to assume a similar morphology would result from FTT processes. Unfortunately, that was incorrect.

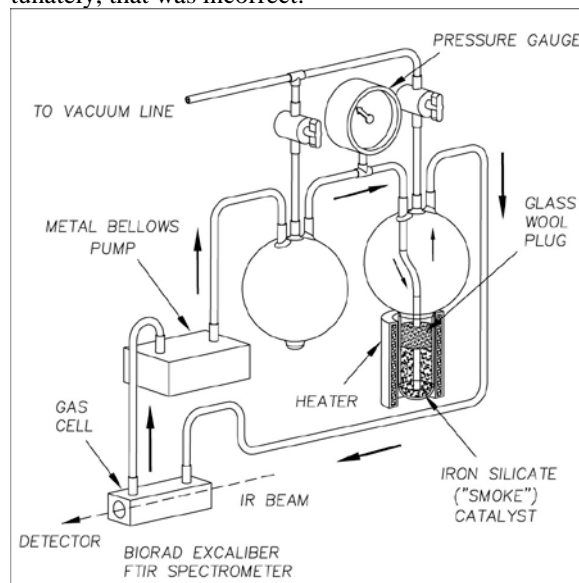


Fig.1. Experimental Catalytic System described in [3].

FTT Reactions on Magnetite: We recently began a series of experiments to quantitatively measure the solid/gas product ratio for the FTT process as a function of catalyst, time, temperature and run number in the apparatus shown in Figure 1 above. Magnetite was selected for these experiments because it is readily available commercially in well defined particle sizes and purities, making our experiments easy to duplicate. For the current set of experiments we used 325 mesh magnetite, 97% (metals basis) from Alfa Aesar. For these experiments, in addition to real time monitoring

of the gaseous species as a function of time via the FTIR spectrometer we also opened the experiment after every fifth run to measure the surface area of the catalyst using a commercial, liquid nitrogen cooled surface area analyzer. Typical results from these measurements are shown in Table 1.

Table 1. Surface area of "magnetite" catalyst

Catalyst	Surface Area (m ² /g)
Initial Magnetite Sample	7.41
Magnetite, 5 runs @450C	19.65
Magnetite, 10 runs@450C	33.95
Magnetite, 15 runs@450C	35.31
Magnetite, 20 runs@450C	49.46

Discussion: The rapid increase in the surface area of the catalyst was very difficult to explain based on our previous experiments and our ingrained assumptions concerning the morphology of the FTT deposited coating. Previous analyses of the FTT grain coating on iron silicate smokes with initial surface area ~125 m²/g and a total mass less than 5 g showed that after 20 runs the grains were 10% by mass carbon and 0.2% by mass nitrogen [6]. Increasing the surface area of our catalyst by a factor of 6 would require more than doubling the average radius of the 325 mesh magnetite catalyst and would require much more than the available quantity of carbon in the system to accomplish this increase. Based on our previous work, we would expect that less than a gram of carbon deposition occurs over 20 runs and we also know that a significant fraction of the available carbon is converted into CH₄ and other organic species via the FTT process [3].

In previous experiments conducted at 600C we have seen the formation and growth of carbon nanotubes [7], essentially a thin string of carbon with a very high surface area per unit mass. However, we have never seen evidence for nanotubes formation at temperatures less than 550C, including both SEM analyses as well as electron diffraction analyses of lower temperature grain coatings [7]. However, in all of the SEM images, the surface always appeared to be "lumpy" – which we attributed to grain clumping and other macroscopic features produced during the FTT process.

Higher resolution SEM images of the much larger magnetite grains tell a very different story. It appears that active regions on the surface of the catalyst initially promote carbon deposition in the local area. However, rather than spreading uniformly over the surface of the grains, the carbon deposit begins to grow away from the catalyst surface. While in some ways this initially appears to resemble VLS (Vapor-Liquid-Solid) growth along a crystalline “c-axis” the resultant deposit is neither crystalline nor is it a smooth needle or whisker: In fact, it is rather clumpy and quite irregular. It also appears that much, if not all, of the deposited carbon is capable of promoting FTT reactions and further carbon deposition. In addition, based on experiments on the formation and growth of nanotubes [7] we know that carbon atoms are relatively easily mobilized from such initial condensates.

Implications for Nebular Dust: We had previously assumed that FTT deposited carbon could be found as a more-or-less uniform coating on nebular grains. However, these results indicate that macroscopic carbon particles many hundreds of nanometers in length and quite irregular in shape could form at least on the surface of magnetite grains, and probably on other surfaces as well. Such growths could have several possible consequences. First, such carbon-rich growths could at least partially replenish pre-solar graphite-like dust previously destroyed in high temperature nebular shocks or lightning strokes. While we know that a large fraction of pre-solar silicate grains were processed in the nebula to produce the much larger dust particles found in meteorite matrix, presolar carbon dust must have experienced similar processes. However, while silicates are converted into vapor or liquid droplets at high temperatures – and these can re-condense – carbon is converted into CO or CO₂ in the oxygen-rich solar nebula. FTT reactions would be one pathway to convert such gases back into the solid carbon species found in meteorites.

An interesting possibility, if such processes occur on the surfaces of larger (mm-scale) silicate and metallic grains in the nebula, is that such growths could act much in the same manner as does fresh snowy condensates on the surfaces of the larger ice grains in Saturn’s rings. Such fluffy “snow” damps out the momentum in colliding particles, changing the coefficient of restitution and promoting grain-grain sticking [8,9]. FTT reactions would happen fastest at the higher temperature, higher pressure regions of the inner solar nebula, just where chondrules, CAIs and other macroscopic meteoritic components are also forming. If some of these refractory surfaces served as catalytic sites for the growth of FTT “whiskers” – whether the clumpy carbonaceous growths observed to grow at 450C, or the

more crystalline carbon nanotubes that readily form at higher temperatures, such surface growths would promote the aggregation of these larger components. In fact, at least one study has reported an association between carbon nanotubes and CAIs [10]. Could such carbonaceous growths be the glue that promoted the growth of meteorite parent bodies?

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