

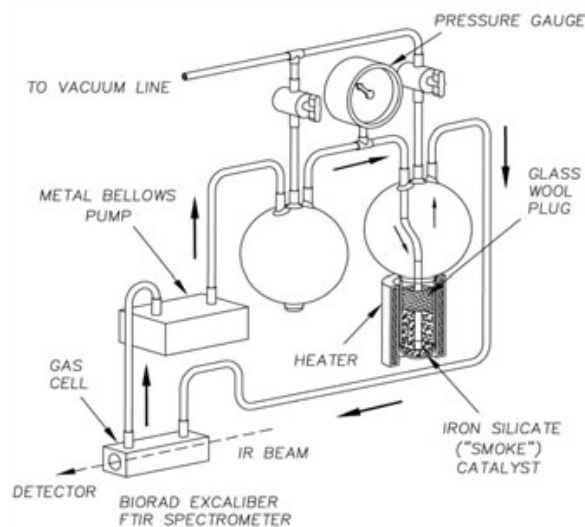
**FISCHER-TROPSCH-TYPE CATALYTIC ACTIVITY IN THE PRIMITIVE SOLAR NEBULA: RESULTS OF NEW EXPERIMENTAL STUDIES USING GRAPHITE AND NOBEL GASES.** Joseph A. Nuth III, NASA's Goddard Space Flight Center, Code 691, Greenbelt MD 20771 (Joseph.A.nuth@NASA.gov).

**Introduction:** The formation of abundant carbonaceous material in meteorites is a long standing problem (Hayatsu & Anders 1981) and an important factor in the debate on the potential for the origin of life in other stellar systems (Hornbeck 1995). Many mechanisms may contribute to the total organic content in protostellar nebulae, ranging from organics formed via ion-molecule and atom-molecule reactions in the cold dark clouds from which such nebulae collapse (Nuth *et al.* 2006), to similar ion-molecule and atom-molecule reactions in the dark regions of the nebula far from the protostar (Ciesla & Charnley (2006), to gas phase reactions in sub-nebulae around growing giant planets (Fegley 1993) and in the nebulae themselves (Pizzarello *et al.* 2006). The Fischer-Tropsch-type (FTT) catalytic reduction of CO by hydrogen was once the preferred model for production of organic materials in the primitive solar nebula (Hayatsu & Anders 1981, Pearce *et al.* 1989, Hindermann *et al.* 1993). The Haber-Bosch (HB) catalytic reduction of N<sub>2</sub> by hydrogen was thought to produce the reduced nitrogen found in meteorites. However, the clean iron metal surfaces that catalyze these reactions are easily poisoned via reaction with any number of molecules, including the very same complex organics that they produce (Kress & Tielens 2003) and both reactions work more efficiently in the hot regions of the nebula. Both of these problems may now be moot.

We have demonstrated that many grain surfaces can catalyze both FTT and HBtype reactions, including amorphous iron and magnesium silicates, pure silica smokes, as well as several minerals (Hill & Nuth 2001). Although none work as well as pure iron grains, and all produce a wide range of organic products rather than just pure methane, these materials are not truly catalysts. The properties of these surfaces change during the course of reaction and become more efficient as the reaction proceeds to build up a macromolecular grain coating that would usually serve to shut down such activity (Johnson *et al.* 2007). Indeed amorphous iron silicate smokes that had accumulated a coating comprising 10% by mass carbon and 0.2% by mass nitrogen based on the total mass of the sample, remained an active and very efficient surface for production of nitrogen-bearing organic materials from a mixture of CO, N<sub>2</sub> & H<sub>2</sub>. More recent work may provide a simple explanation for these observations: the carbonaceous grain coating is itself an efficient surface for the

reduction of CO and N<sub>2</sub> by hydrogen to form a variety of organic materials.

**Experimental Description:** Llorca & Casanova (2000) demonstrated that FTT reactions occur under low pressures typical of the primitive solar nebula. Our experiments were designed to produce mixtures of solids and organics that could serve as analogs of primitive asteroidal material. Grains in protostellar nebulae are exposed to the ambient gas for hundreds or even tens of thousands of years at pressures ranging from 10<sup>-3</sup> to 10<sup>-4</sup> atm or less. We do not have such times available for laboratory experiments, although we can duplicate the total number of collisions a grain might experience with components of the ambient gas by running experiments for shorter times at higher pressures. In our laboratory, experiments last from about 3 days at temperatures of 873 K to more than a month at temperatures of 573 K. If an average experiment lasts a week (6.05 × 10<sup>5</sup> s) then we can simulate two centuries (6.3 × 10<sup>9</sup> s) of exposure to an ambient gas at 10<sup>-4</sup> atm, by running experiments at ~1 atmosphere total pressure. Although these higher pressures could conceivably effect the products synthesized in our experiments, we believe that the effects of temperature are much more important.



**Figure 1.** Simple experimental apparatus used to circulate reactive gas mixtures over potential catalysts at controlled temperatures and monitor the changes in the circulating gas via infrared spectroscopy.

The experiments were very simple (see Figure 1 and Hill & Nuth 2003). We load ~25 cm<sup>3</sup> of catalyst into a glass finger through which gas can circulate by

means of a glass tube that extends to the bottom of the finger. The finger is heated via an external mantle to a controlled temperature. We evacuate the system to a pressure less than  $\sim 0.1$  Torr, then fill the system with gas (75 Torr CO, 75 Torr N<sub>2</sub>, 550 Torr H<sub>2</sub>) to a total pressure of 700 Torr. For noble gas trapping experiments we first add 25 torr of a noble gas mixture consisting of 49% Ne, 49% Ar, 1% Kr and 1% Xe) We then begin to circulate gas using a bellows pump, begin heating the finger containing the catalyst and record our first infrared spectrum of the gas (only CO is detected in this spectrum) using an FTIR spectrometer. The gas fluidizes the catalyst. The finger is plugged at the top using glass wool to contain the grains while letting the gas circulate. As the experiment proceeds we use periodic FTIR spectra to follow the loss of CO and the formation of methane, water, and carbon dioxide, and monitor smaller spectral features due to ammonia and N-Methyl Methylene Imine.

Once the CO has been reduced to about ten percent of its starting concentration we take a final infrared spectrum, turn off the heater, cool the system to room temperature, evacuate it to less than  $\sim 0.1$  Torr, then refill the system with fresh gas and begin a second run. Note that we do not use a fresh batch of catalyst for this second run. By making  $\sim 15$  runs with the same catalyst, we simulate  $\sim 3,000$  years exposure of grains to nebular gas and build up a substantial coating of macromolecular carbon, nitrogen, & hydrogen.

**Previous Results:** For a typical, textbook catalyst, this result is counterintuitive. With each additional run, the catalyst forms slightly larger clumps (thus reducing surface area), the active metal atoms at the surface become more oxidized due to reaction with water generated by the FT reaction, some reactive sites on the catalyst become coated by the macromolecular carbon generated in previous runs and some catalyst simply gets trapped in the glass wool and is lost to the system. Each of these factors should slow reaction rates in subsequent experimental runs, yet we observe an increased rate of reaction after the first few runs, followed by a steady rate thereafter. The best explanation for all of these observations, including the large mass fraction of carbon and nitrogen deposited onto the grains after  $\sim 20$  runs, is that the macromolecular carbonaceous coating is a better catalyst than the inorganic sites it covers. This has consequences for FTT reactions in protostellar nebulae.

**New Experimental Results:** We have used graphite in place of the amorphous silicate catalyst and we observe essentially the same results. The system requires at least 5 or 6 experimental runs to reach a steady state rate of reaction as measured either by CO depletion or methane generation at 873K. we are cur-

rently examining the reaction products using TEM and will report the results at this meeting.

We also did experiments to measure the trapping of a noble gas mixture in the growing carbonaceous layer. We performed these experiments at 873K using an amorphous iron silicate catalyst, even though we expect the high temperature to inhibit the trapping of the gas into the growing carbonaceous layer. Doing experiments at lower temperatures is certainly possible, but we did not have sufficient time to complete low temperature experiments and do the analysis prior to the LPSC. We plan to present the results of our experiments and a comparison to Phase Q noble gases.

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