DIFFICULTIES AND SOLUTIONS IN MEASURING THE RATES OF SURFACE-MEDIATED REACTIONS SUCH AS THE FISCHER-TROPSCH TYPE REACTION. J. A. Nuth¹ N. M. Johnson2 and F. T. Ferguson2,3, ¹Solar System Exploration Division, Code 690, NASA Goddard Space Flight center, Greenbelt MD 20771 USA joseph.a.nuth@nasa.gov, ²Astrochemistry Branch, Code 691, NASA-GSFC, Greenbelt MD 20771, ³Chemistry Department, The Catholic University of America, Washington DC 20064.

Introduction: Carbonaceous dust and silicate grains are intimately mixed in the interstellar medium [1,2]. Prior to being incorporated into new protostars, the association of carbonaceous materials and silicates becomes even more intimate through the formation of carbonaceous coatings on the dust in Giant Molecular Clouds [3]. Until recently there has been little consideration of exposing such a mixture to conditions in the evolving nebular environment. It has been estimated [4] that more than 95% of all pre-solar silicates were vaporized or melted in the primitive solar nebula. This implies that at least 95% of the pre-solar carbon dust was also destroyed (converted into CO or CO2) during these same high temperature events. Yet solar system bodies are not greatly depleted in carbon and therefore at least one mechanism must be available in nature to convert highly volatile CO or CO2 into carbonaceous solids that can then be accreted by planetesimals. We have previously suggested [5] that Fischer-Tropsch-Type (FTT) surface mediated reactions could easily convert the CO or CO2 produced in high temperature nebular events back into carbonaceous solids that could be incorporated into planetesimals. This same mechanism may also trap planetary noble gases into these carbonaceous solids [6].

We are not claiming here that Fischer-Tropsch Type (FTT) reactions constitute the single – or even the most important - mechanism that forms the full distribution of organic molecules in asteroids or comets or that are found in meteorites or IDPs. There are many different processes that can be important sources for particular compounds in many different meteorite types [7]. However, we do believe that FTT reactions are the most efficient, but certainly not the only; mechanism for converting nebular CO or CO2 into solid carbonaceous materials that are easily incorporated into planetesimals and that could then serve as the feed stock that is transformed by various thermal or hydrothermal processes into the myriad organic molecules found in natural sources.

While we use industrial reactions as models of nebular processes; e.g., the Fischer-Tropsch reaction: CO + 3H2 => CH4 + H2O; the Haber-Bosch reaction: N2 + 3H2 => 2NH3; the water-gas shift reaction: CO + H2O => CO2 + H2; or the Boudouard Reaction: 2CO => CO2 + Csolid, natural reactions on grain surfaces in the protostellar nebulae are much more complex. In our simple experimental system, starting with a mixture of CO + N2 + H2 we find a wealth of products including CH4, CO2, H2O, C2H6, alkanes, aromatics, nitriles, amines, aldehydes, ketones, PAHs, and kerogens, among others [8,9]. The specific ratios of this wide range in natural products depend on time, temperature, pressure, the catalyst used in the experiment, the previous reaction history of the system, etc. In the more complex and continuously changing environment of a protostellar nebula, an even more diverse set of products might be expected. For this reason it can be extremely misleading to discuss a specific model reaction in isolation when describing natural reactions that might occur on the surfaces of grains in the Solar Nebula. Hereafter we will simply discuss measurements of Surface Mediated Reactions.

Figure 1. Experimental apparatus used to monitor the progress of the reaction: CO + N2 + H2 => products.

Reaction Rate Measurements: Our experimental system (Figure 1) was designed to monitor the products of surface mediated reactions starting from a simple mixture of CO + N2 + H2. We have measured the rate at which CO decays or at which CH4 is formed quantitively, using the HITRAN spectroscopic data base [10] and have previously discussed the problems found in scaling the gas phase reaction rates to the surface area of the catalyst, as the surface area of these grains continuously increase due to reactions with the gas. Not only does the surface area of an individual catalyst change during the reaction via growth of filamentary carbonaceous tubes, but the ratio of surface
deposited carbon to gas phase carbon products also changes as a function of grain composition, time and temperature [11,12]. One solution for this problem is to measure the initial rates of reaction on the surface of a catalyst and to stop the experiment before the surface properties have changed too much. Results for this type of measurement are shown in Figure 2 where the catalyst was a length of pure iron wire. Measurements per unit surface area for different lengths of wire were in rough agreement; however, these experiments show a completely new problem. While the rates for the CO loss scale reasonably well with the surface area of iron wire, the 325 mesh iron powder is much less reactive per unit surface area, yet both are pure iron.

![Catalyst Reaction Rates - 773 K](image)

Figure 2. A plot of the relative loss of CO as a function of time scaled to the surface area of the catalyst.

**Scaling by Surface Area:** The experimental system shown in Figure 1 was set up as a fluidized bed reactor in which the gas injected at the bottom of the catalyst bed “liquefies” the very fluffy iron silicate smokes that we first tested as catalysts. In such a system the gas interacts freely with the entire catalyst bed. Use of the much denser iron, hematite or goethite powders in this system eliminates the fluidity of the catalyst at the gas flow rates available in our system and even though we thought that the gas permeated the entire bed, it is obvious from Figure 2 that a significant portion of the iron powder catalyst did not participate in the reaction. While this does not change the product distribution of the reactants we previously reported, it certainly effects measurements of the reaction kinetics.

We have begun a new set of experiments using iron wire as a catalyst. We will report measurements of the initial reaction rate per unit surface area, order of the reactions and activation energy for the initial reaction of CO + N₂ + H₂ → products as a function of temperature and time. We will also measure the change in the surface area of the wire catalyst as a function of the reaction number between experimental runs. While our previous experiments demonstrated more than a six-fold increase in surface area for an iron powder catalyst over the course of 20 reactions, we now consider this to be a lower limit, as the surface area per gram was measured for a randomly drawn sample of the bulk material while the majority of the potential iron grains had minimal interaction with the gas. These experiments should yield a much better estimate for the relative rate of growth of the surface area of the catalyst as a function of the extent of the reaction.