A SELF-PERPETUATING CATALYST FOR THE PRODUCTION OF COMPLEX ORGANIC MOLECULES IN PROTOSTELLAR NEBULAE

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ABSTRACT

When hydrogen, nitrogen, and CO are exposed to amorphous iron silicate surfaces at temperatures between 500 and 900 K a carbonaceous coating forms via Fischer-Tropsch-type reactions. Under normal circumstances such a coating would impede or stop further reaction. However, we find that this coating is a better catalyst than the amorphous iron silicates that initiate these reactions. Formation of a self-perpetuating catalytic coating on grain surfaces could explain the rich deposits of macromolecular carbon found in primitive meteorites and would imply that protostellar nebulae should be rich in organic material.

Subject headings: astrobiology — astrochemistry — methods: laboratory — molecular processes — solar system: formation — stars: pre–main-sequence

Online material: color figure

1. 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). Large quantities of complex prebiotic materials could greatly simplify chemical evolution in planetary environments starting from a rich organic broth and leading to the simplest forms of living organisms. 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 subnebulae around growing giant planets (Fegley 1993) and in the nebulae themselves. It is unclear that any of these mechanisms could produce enough material to account for the relatively large quantities of organics found in the most primitive meteorites (Pizzarello et al. 2006).

The Fischer-Tropsch-type (FTT) catalytic reduction of CO by hydrogen to produce methane and other hydrocarbons was once the preferred model for production of organic materials in the primitive solar nebula (Hayatsu & Anders 1981; Pearce et al. 1989; Hindemann et al. 1993). The Haber-Bosch (HB) catalytic reduction of N₂ by hydrogen to make ammonia was thought to produce the reduced nitrogen found in meteorites. Both FTT and HB-type reactions have a major Achilles’ heel when operating in the “dirty” environment around a protostar: 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 2001). In addition, both FTT and HB-type reactions work much more efficiently in the hot innermost regions of the nebula rather than in the cooler, lower pressure environments where the asteroids—parent bodies for most meteorites—may have formed. Both of these problems may now be moot.

We have demonstrated that many grain surfaces can catalyze both FTT and HB-type reactions, including amorphous iron and magnesium silicates, pure silica smokes, and several minerals (Hill & Nuth 2003). Although none of these materials 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 (Gilmour et al. 2002) remained an active and very efficient surface for production of nitrogen-bearing organic materials from a mixture of CO, N₂, and H₂. 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 N₂ by hydrogen to form a variety of organic materials.

2. EXPERIMENTAL DESCRIPTION

Llorca & Casanova (2000) demonstrated that FTT reactions occur under low pressures typical of the primitive solar nebula. Our experiments were designed to test the relative efficiency of various potential catalytic materials and to produce mixtures of solids and organics that could serve as analogs of primitive asteroidal material for later experiments. Grains in protostellar nebulae are exposed to the ambient gas for hundreds or even tens of thousands of years at pressures ranging from 10⁻³ to 10⁻⁴ 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 × 10⁵ s), and if the only consideration for simulating the effects of the reaction is the total number of collisions of...
potential reactants with the catalytic surface, then we can sim-ulate two centuries \((6.3 \times 10^9 \text{ s})\) of exposure to an ambient gas at \(10^{-4} \text{ atm}\) by running experiments at \(\sim 1 \text{ atm}\) total pressure. This scaling assumes that the reactants strongly bind to the surface of the catalyst and that this is the rate-controlling step. While it is true that the CO and N\(_2\) must be strongly bound in order to weaken their bonds and thus increase their rates of reaction with H\(_2\), we are not certain that this is the rate-controlling step, although Kress & Tielens (2001) deduced that it must be. If the rate-controlling step is the reaction of H\(_2\) with the CO or N\(_2\) bound on the grain surface, then the important consideration is now the number of collisions of H\(_2\) with the CO or N\(_2\) bound on the catalyst rather than the number of collisions of CO or N\(_2\) with the catalyst, and reaction time can once again be scaled to the number of collisions.

The situation becomes even more complicated if the CO and H\(_2\) must “meet” at an active site on the catalyst surface. This scenario would be more like reactions that occur in the gas phase: the number of reactive collisions would therefore scale as the square of the total gas pressure. In our opinion, this is a worst case scenario as long as the reactants interact strongly with the catalytic surface. However, if true, then the week-long experiments discussed above would be the equivalent of 2 million years of nebular exposure rather than the 2 hundred years that we propose. In addition, doing experiments at pressures near 1 atm could conceivably affect the products synthesized in our experiments. We believe that the effects of temperature are much more important, but to avoid any minor effects due to changes in total pressure or due to changes in the relative partial pressures of the reactants we ran all of the experiments reported below with the same gas mixture and the same starting pressure: 75 torr CO, 75 torr N\(_2\), and 550 torr H\(_2\) (700 torr initial pressure).

The experiments themselves were also very simple; see Figure 1 (Hill & Nuth 2003). We first load \(\sim 25 \text{ cm}^3\) 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 temper-

3. RESULTS

Figure 2 (top) shows loss of CO with time for runs at \(\sim 873 \text{ K}\). The CO decays more slowly in the first run than in subsequent runs. The generation of methane as a function of time and run number is shown in Figure 2 (bottom); again, the rate is slower in the first run, but gets faster for subsequent runs. All gas-

Fig. 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.

Fig. 2.—Top: Changing abundances of CO as a function of time in four separate runs using the same catalyst. Bottom: Changing abundances of methane in successive experimental runs at \(873 \text{ K}\) using the same catalyst. [See the electronic edition of the Journal for a color version of this figure.]
phase products, with the exception of CO$_2$, follow the pattern set in Figure 2 (bottom) by methane in experiments carried out at 573, 773, and 873 K. CO$_2$ peaks, then decreases (depending on temperature), as the CO abundance declines below ~25%–30% of its initial level. At low levels of CO, the CO$_2$ is converted back into CO on the grain surfaces, slowing the apparent decay of CO, as is observed. All of our experimental runs followed this same pattern, with a much slower rate of change at lower temperatures, but a general increase in reaction rate after the catalyst was first exposed to the reactive gas. With more efficient catalysts and higher temperature experiments, the system quickly achieves the final “steady state” reaction rate.

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 FTT 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. One explanation for all of these observations, including the large mass fraction of carbon and nitrogen deposited onto the grains after ~20 runs, is that the macromolecular carbonaceous coating is a better FTT catalyst than the inorganic sites it covers. This hypothesis has several interesting consequences for FTT reactions in protostellar nebulae.

4. DISCUSSION

If the macromolecular coating itself promotes FTT and HB-type reactions, then there is no barrier to the deposition of a thick, multilayer organic coating on any grain surface. With traditional catalysts, no more than a monolayer can be deposited on a grain surface before the reaction stops; however, if the coating itself is a catalyst then one layer promotes the formation of the next, ad infinitum. If the macromolecular coating forms on any grain surface, even at very different rates, then all grain surfaces will eventually be coated and large quantities of CO, N$_2$, and H$_2$ will be fixed onto grain surfaces as a macromolecular organic coating. We note that it is much easier to incorporate such carbonaceous coatings into asteroidal parent bodies than it is to trap the more volatile products of traditional FTT or HB-type reactions such as methane or ammonia into these same bodies, since FTT and HB processes proceed more rapidly at higher temperatures and pressures, e.g., in the innermost regions of protostellar nebulae where layers of organic material could be quickly deposited onto grain surfaces.

We do not know why the carbonaceous grain coating is a better catalyst than the inorganic sites it covers. Metals within the silicates might remove electron density from the CO or N$_2$ better catalyst than the inorganic sites it covers. This hypothesis has been quickly deposited onto grain surfaces.

5. SUMMARY

Laboratory experiments have demonstrated that a macro-
molecular, nitrogen-rich, organic coating forms on the surfaces of many different grain types and that this coating efficiently promotes the conversion of CO, N$_2$, and H$_2$ into additional layers of organic material. Such grain coatings could have been efficiently incorporated into growing planetesimals and would then be modified by heating, hydration, and other lithification processes that produced the modern population of asteroids and meteorites. Much more experimental work is required to understand the metamorphism of the initial organic materials con-
tained within various types of evolving planetesimal, and the analogs produced in these experiments are intended for such experiments. However, finding an organic coating that will naturally form under conditions in protostellar nebulae, and that will continue to grow as long as it is exposed to a CO, N₂, and H₂ rich gas at moderately high temperatures, adds an entirely new dimension to the chemistry of these nebulae. The organic content of protostars can no longer be modeled as the remnant organic coatings on grains from parent dark molecular clouds, even with the addition of new materials formed by similar processes in the cold dark interiors of such nebulae. One must now account for abundant organic material produced in the innermost regions of these nebulae and transported outward, possibly to the Kuiper Belt and beyond, by the same mechanisms that brought crystalline grains and fragments of chondrules and CAIs to comet Wild 2.

REFERENCES