

PARTICLE GENERATION AND EVOLUTION IN SILANE (SiH₄) /ACETYLENE (C₂H₂) FLAMES IN MICROGRAVITY

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INTRODUCTION

The objective of this experimental program is to advance the understanding of the coupling of particle formation with gas phase combustion processes. The work utilizes the unique SiH₄/C₂H₂ combustion system which generates particulate products ranging from high purity, white SiC to carbonaceous soot depending on equivalence ratio (Ref. 1). A goal of this work is to identify gas phase or particle formation processes that provide the enthalpy release needed to drive the combustion wave, and to locate the steps of the particle formation process that determine SiC stoichiometry and crystallinity. In a real sense, these SiH₄/C₂H₂ flames act like "highly sooty" hydrocarbon flames, but with simpler chemistry. This simplification is expected to allow them to be used as surrogates to advance understanding of soot formation in such rich hydrocarbon flames. It is also expected that this improved understanding of SiC particle generation and evolution in these self-sustaining flames will advance the commercial potential of the flame process for the generation of high purity SiC powders.

BACKGROUND

We previously investigated SiH₄/C₂H₂ flames in constant volume combustion experiments. In that work (Ref. 2), we found that SiH₄/C₂H₂ flames propagate over a wide range of stoichiometry ratios from 0.05 (C₂H₂-rich) to 2.5 (SiH₄-rich). Burning velocities extracted from the pressure histories of combustion events exhibited an unusual double maximum as a function of the SiH₄/C₂H₂ reactant ratio. The major products of the combustion are H₂ and fine powder containing most of the reactant mass of carbon and silicon. For a narrow range of SiH₄/C₂H₂ mixture ratios near 2.0 (equal silicon and carbon atomic concentrations), the powder product of the combustion was found to be stoichiometric, nanocrystalline, cubic silicon carbide (SiC), consistent with intimate mixing on the atomic level. Processes which can contribute to the production of the silicon carbide powder include parallel formation of silicon- and carbonaceous particles that agglomerate with rapid interparticle diffusion to produce stoichiometric SiC; formation of silicon- (or carbonaceous) nuclei which grow by chemical vapor deposition with the proper ratio of gas phase Si_xH_y and C_xH_y species; or direct condensation of Si_xC_yH_z on SiC nuclei. We have presented evidence (Ref. 2) for coupling of the silicon and carbon chemistries, i.e., that the silicon-carbon bonds form early in the flame and suggested that the such gas phase species determine the stoichiometry and crystallinity of the final product, indicating an important role of the third process. The kinetics of the overall mechanism is important in propagating the flame. Based on available thermochemical data for known and predicted gas phase intermediates, most of the combustion energy (~80%) is released in the particle formation processes.

Insight into the mechanism of SiC formation may be gained through comparisons of flame data and the product properties for a series of related flames. It is difficult to obtain detailed flame structure information from the constant volume combustion experiments described above. A steady-state, burner-supported flame is more suitable for accurate flame

diagnostics. In the present microgravity studies, the complex effects of buoyancy, buoyancy induced mixing, and gravitational settling are substantially reduced or eliminated, giving rise to undistorted and steady flames that reflect the combustion chemistry and particle formation processes. Accurate correlations are expected among, e.g., reactant stoichiometry, added gases, burning velocities, flame temperatures, and the resultant powder properties. Particle formation and growth mechanisms and their coupling will be addressed in this work.

EXPERIMENTAL APPROACH AND DESIGN

The program focus is on fundamental flame properties (burning velocity, particle and gas temperatures, flame species, and product characterizations). The key experimental challenges are to make reliable burning velocity measurements and to make measurements (e.g., gas/particle temperatures, concentrations) near the flame front to relate to the burning velocities of these particle-laden premixed flames. To make burning velocity measurements that reflect the adiabatic combustion chemistry, energy loss and thermophoretic transport to the burner must be minimized. In addition, flame front diagnostics require a geometry in which the pre-flame region is not obscured by the highly luminous particle cloud. A useful geometry that satisfies these requirements is that of inverted cone flame stabilized above a rod coaxial with the reactant flow and extending out of the burner outlet. The angle the flame makes relative to the flow direction is related to the ratio of the flow and to burning velocities. A related geometry is a "vee" flame stabilized above a transverse rod downstream of the burner outlet.

The $\text{SiH}_4/\text{C}_2\text{H}_2$ combustion system presented challenging design issues which have been addressed. The major features of the resultant design are described here. Both the reactants and the flame products are flammable and must be isolated from air exposure. The pyrophoric properties of the SiH_4 reactant are of particular concern, and for safety reasons, the allowable onboard quantity is limited. H_2 , the gas phase flame product, also presents potential hazards related to its wide flammability limits in air. Because neither can be exposed to air, the apparatus design provides for the entire experiment to be performed in a sealed N_2 -filled system. Means to maintain a constant pressure flame environment in the burner chamber is provided by a large back-pressure regulator connected to a dump tank which is evacuated before the experiment. To prevent N_2 bleed from the atmospheric pressure flame chamber through the regulator into the evacuated dump tank before the drop is initiated, they are separated by a high Cv solenoid valve which is opened only when the burner and N_2 (shroud and auxiliary chamber) flows begin. Both the solenoid valve and the back-pressure regulator are protected from the silicon carbide powder product with a high throughput, high efficiency filter. To assure safe operation in the unlikely event of a chamber seal failure during the experiment, the flame product H_2 is diluted with N_2 to below its flammability limit. The total quantity of onboard pressurized gas (N_2 , SiH_4 , and $\text{SiH}_4/\text{C}_2\text{H}_2$ reactant mixture) is limited so that the chamber pressure cannot exceed its pressure rating with complete gas release into the chamber and complete reaction of the reactants.

The reactant $\text{SiH}_4/\text{C}_2\text{H}_2$ mixtures will be prepared (by partial pressure) and stored in a reservoir with a feed line to the burner. To assure complete use of the reactant mixture (and hence to minimize the total quantity required), an inert flexible bag in the reservoir will be inflated with N_2 "piston" gas, feeding the reactant mixture to the burner by displacement. Constant mass (molar) flow of the piston gas will be provided by regulating the fixed pressure

upstream of critical flow orifices. The molar feed rate of the reactant mixture is essentially equal to that of the piston gas. When not being fed to the burner, the reactants and the piston bag will be isolated in the reservoir by solenoid valves. The reservoir will have a high pressure rating to withstand unintended ignition of the stored mixture.

DESIGN VALIDATION EXPERIMENTS

A laboratory prototype apparatus was assembled to test the design concepts and as a design aid for the microgravity drop tower apparatus. Normal gravity experiments investigated the feasibility of rapidly (~1 sec) establishing a steady flame in simulated drop experiments. One of the major questions was whether the back pressure regulator could maintain chamber pressure stable enough that steady flames could quickly be established in the presence of flow changes comparable to those expected in the microgravity experiments. For the initial laboratory experiments, we chose to use CH₄(methane)-air "vee" flames supported above a transverse rod at the exit of a 3 cm diameter nozzle burner. The CH₄-air flames have comparable burning velocities to those previously measured for SiH₄/C₂H₂, without the complication of producing particles which would need to be filtered upstream of the back-pressure regulator. The burner was housed in a 15 cm (6") diameter Pyrex cross (~10 L), and the flame was viewed and recorded with a video camera through a window on one of the 10 cm (4") diameter side arms. The product gases from the chamber were exhausted into an evacuated 30 L tank through a solenoid valve and the dome-loaded back pressure regulator (Tescom 26-2900). The other critical aspect of the design is the burner feed method. As planned for the microgravity experiments, premixed burner reactants (CH₄-air) were displaced from a constant volume reservoir by filling a flexible bladder in the reservoir with a constant mass flow rate of N₂ supplied through a critical orifice. To maintain constant volume flow rate through the burner, it was critical that the chamber pressure remain constant. If the chamber pressure momentarily exceeded the reservoir pressure, the burner flow rate decreased and even reversed.

Experiments clearly showed that flow restrictions must be minimized between the chamber and the back pressure regulator for the regulator to function optimally. The experiments confirmed that the response and throughput of the back pressure regulator was sufficient to dampen out pressure pulses (the largest are generated by the ignition of the flames) to minimize burner flow attenuation. For comparison, near-stoichiometric (9% CH₄ in air) flames were ignited and attached in under 1 second from initiation of flow (~600 scc/s) from the reservoir to the burner. Leaner flames (6.5% CH₄) have half the burning velocity and were fed at ~300 sccs. Attached flames were observed in about 1 second. Rich flames with comparable experimental burning velocities to the lean flames (i.e., 12.9% CH₄) required longer times (> 2 seconds at the same flow velocities) to stabilize. This behavior would make the intended microgravity measurements more difficult.

To better understand the observed differences in the lean and the rich flame ignition behavior, recorded chamber pressures and flame images were compared. From the pressure records, it was found that the rich mixture experiments showed larger pressure excursions in the ignition period than the lean mixtures. The flame images revealed that once they were stabilized, the standoff distance of the rich flames above the flame holder was larger than that of the lean flames. The distance fluctuated periodically (15-30 Hz). It is likely that the two sets of

observations (pressure and flame fluctuations) are related and not coincidental. The flame holding observations can be understood on the basis of Lewis number effects.

Sung, Law, and Umemura [Ref 3] investigated inverted flame stabilization of C₃H₈(propane)-air flames and found differing behavior of lean and rich flames. For the rich flame, the height above the holder that the flame adopted was nearly independent of flow velocity, while the lean flame was stabilized over a wide range of heights above the holder, even though the laminar burning velocities of the two mixtures are nearly identical. A similar behavior characterizes our observations from the 6.5% and 12.9% CH₄-air flame recordings. However, in our case, the lean flame was stabilized at a fixed height, and the rich flame standoff distance fluctuated widely. These trends are seen to be identical if one compares the dimensionless Lewis numbers, Le, characteristic of the reactant mixtures. Sung et. al. calculate Le as the thermal diffusivity of the mixture divided by the mass diffusion coefficient of the deficient reactant (the inverse is also used by others). In their nomenclature, the observations are: rich C₃H₈/lean CH₄ - Le < 1 (small, stable standoff distance); lean C₃H₈/rich CH₄ - Le > 1 (large, variable standoff distance). Sung et. al. argue that the latter case is amenable to "adiabatic stabilization" when positioned at a great distance from the holder (heat sink). We also found the Le>1 flame to be susceptible to "waving" motions. These instabilities and the large pressure excursions we observed with these rich CH₄ flames are probably related to the "weaker" flame stabilization. Similar behavior could require longer microgravity times (as available in the 5 second drop tower) to stabilize the SiH₄/C₂H₂ flames in planned experiments. We estimated (Ref 4) that SiH₄ and C₂H₂ have similar thermal diffusivities (0.088 cm²/s) and self-diffusion coefficients (0.11 cm²/s). The computed Lewis number is less than 1 (Le ~ 0.81) for both rich and lean flames. The Lewis number predicts a tendency to stabilize near the holder (non-adiabatic). Thus, a more stable flame would be observed, but in the vicinity of the holder surface. It is not clear how valid this is for stoichiometric SiH₄/C₂H₂ mixtures. We are pursuing experimental measurements to answer this question.

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