Chemical Physics Letters 570 (2013) 104–108

Contents lists available at SciVerse ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Formation of chain aggregates in external electric field

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ARTICLE INFO

Article history:
Received 20 February 2013
In final form 21 March 2013
Available online 1 April 2013

ABSTRACT

Influence of an electric field on formation of aggregates has been studied by filling a cell containing carbon grids with products of combustion of methane in air with silica admixture. After exposing during 1 h to the combustion products, the grids were removed and analyzed using Transition Electron Microscopy (TEM) technique. When a voltage of 5 kV was applied between electrodes in the cell, the 'fiberlike' structures were formed. No 'fiberlike' structures were observed when the voltage was switched off. The estimations based on the simple theory of interaction between the induced dipole momenta were performed to explain the present observations.

1. Introduction

Flames are convenient environments for producing diverse materials because the physical and chemical processes proceed there rapidly due to high temperatures. In particular, flames are widely used for production of powders [1,2]. At the first stage of this process the growth of liquid particles is a result of coagulation and attachment of nucleating molecules to these droplets. When these particles enter a cold part of the flame, they become solid, and then the subsequent growth due to joining of solid particles leads to formation of fractal structures.

It was observed experimentally [3,4] that electric fields can have great influence on the processes of growth of the particles in flames. This influence was attributed mainly to changing the flame properties by the electric field such as decreasing flame thickness [4] or charging particles in high temperature environment [3]. The growth process has another character if it proceeds in an external electric field at low temperatures. In this case the growth of structures occurs through interaction of dipole moments induced by an external electric field. At large density of a nucleating admixture, fractal fibers are formed if the growth process lasts sufficiently long [5,6]. The peculiarity of this process is that formed structures are directed along the electric field, and new particles attach to the ends of the growing structure. The goal of this Letter is comparison of experimental and theoretical results for the fiber growth when created in a flame silica aggregates are introduced in a cell exposed to high voltage.

2. Experimental study of silica aggregate formation under applied electric field

The silica aggregates were produced in a flat stoichiometric methane/air flame burning at atmospheric pressure and stabilized above the ceramic surface. In the present experimental setup the burner head had diameter of 6 cm. To stabilize the flow, a tube with diameter of 8 cm was installed at height 10 cm above the burner. The total flow rate of the stoichiometric methane/air mixture was 620 cm^3/s that corresponds to the total thermal power of 2 kW, the mass flux $\rho v = 0.025$ g/(cm^2 s) and exit velocity of 22 cm/s. The flame temperatures were determined by solving governing equations describing one-dimensional burner-stabilized flames using the PREMIX code from the Chemkin II suite [7] with GRI-Mech 3.0 chemical mechanism [8]. It should be pointed out that these 1-D calculations do not take into account heat losses due to radiation and mixing combustion products with surrounding air and thus are only valid at a limited zone above the burner deck. Therefore, additionally to the calculations, the flame temperature was also determined experimentally by fitting the measured spontaneous Raman scattering spectra of nitrogen. Details of the optical experimental setup can be found in [9]. The measured and calculated temperature profiles are shown in Figure 1. The measured flame temperature reaches its maximal value at a very short distance (3 mm) from the burner deck, remains constant up to 3 cm and then gradually decreases. As can be seen, there is an excellent agreement between the measured and calculated profiles for heights up to 2–3 cm above the burner deck. The disagreement at heights $h > 3$ cm can be explained as was already mentioned above by heat losses to the surroundings and mixing with ambient air. The measured radial temperature and main species profiles at

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http://dx.doi.org/10.1016/j.cplett.2013.03.061

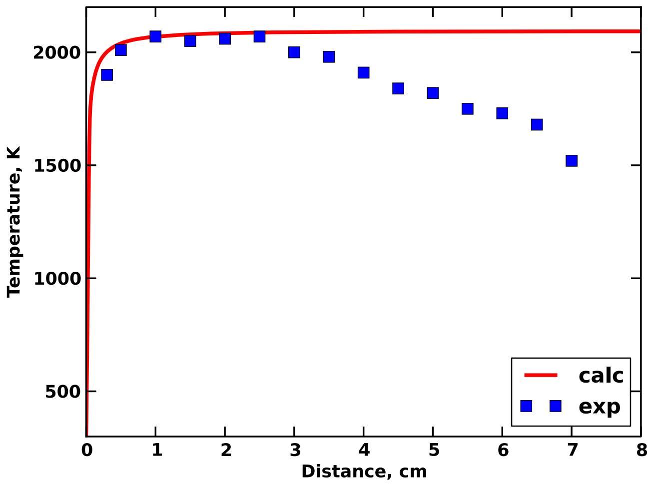

Figure 1. Calculated and measured temperature profiles in CH_4/air flame.

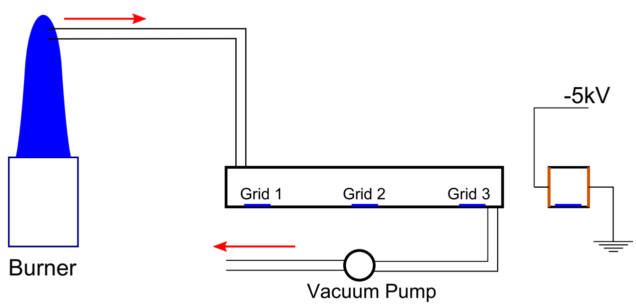

Figure 2. Scheme of experimental setup for the flame in an external electric field.

height of 7 cm are much narrower than those measured close to the burner deck but are still uniform up to distance of 1 cm from the axis. Thus diffusion of the surrounding air is still insignificant in the domain $r < 1$ cm and flow can be considered one-dimensional.

Hexamethyldisiloxane $C_6H_{18}Si_2O$ (abbreviated as L2) was added to the unburned air/gas mixture by blowing methane through liquid L2. The concentration of L2 in the unburned air/gas mixture was estimated to be 250 ppm by weighting the consumed liquid L2 during long (1 day) continuous operation.

The schematic of the experimental setup for study of the influence of the electric field on the growth of fractal structures is shown in Figure 2. The silica aggregates were sampled using a probe with an orifice of 0.2 mm, cooled in a cold water bath to remove water from combustion products and flushed through a cell of 50 cm length and rectangular cross section of 2×2 cm^2. The cell was connected to the sampling probe by a Teflon tube with the inner diameter of 6 mm and length of 2 m. The pressure inside the cell was close to atmospheric (about 800 mbar). Two opposite sides of the cell are made from copper and other two opposite sides are made from perspex. Voltage of up to 5 kV has been applied to the copper plates. Grids made from carbon coated copper were placed inside the cell for collecting silica particles for subsequent TEM analysis. The grids were analyzed using a Jeol 2010F electron microscope operated at 200 kV. Two types of experiments were conducted in the present work. In the first experiment, the grids were placed into the middle of the cell. The cell was flushed during 10 min by combustion products containing silica aggregates. Then the cell was closed and the grids were removed from the cell after 1 h exposure time. In the second experiment the grids were placed close to entrance and exit of the cell. After flushing the cell during 15 min by combustion products, the grids were removed.

Both experiments were performed twice: with and without applied voltage of 5 kV. Typical TEM images of the surfaces of the grids placed in the middle of the cell and exposed during 1 h with and without electric field are shown in Figures 3. As can be seen, the structure of silica aggregates on the left and right images is very different. The aggregates extracted from the cell without applied electric field have typical form of fractal structures with the size less than 1 μm. The aggregates extracted from the cell with applied electrical field are larger, with the size of 5–10 μm and have 'fiberlike' structure composed from small 'needlelike' aggregates. Clearly, electric field enhances formation of large aggregates. The separate 'needlelike' aggregates are also found in the samples obtained with applied electric field. A typical 'needlelike' aggregate is shown on left side of Figure 4, where the TEM image is zoomed four times (left image) in comparison with Figure 3. For comparison, a typical aggregate from the sample taken without applied electric field is shown on right side of Figure 4 with zoom 10×. While the left image exhibits the elongated particle with length of ~3 μm, the shape of the aggregate without electric field is that of a typical fractal structure.

The efforts to specify the influence of the electric field on a shorter time scale by carrying out the second experiment were so far unsuccessful. It was expected to see the differences in sizes and morphology because particles falling on the grid placed at the entrance are not exposed to the electric field while particles collected by the 'exit' grid are exposed to electrical field during their drift inside the cell. Unfortunately, no substantial differences in the sizes and structures of the aggregates are observed in images obtained with and without electric field (see Figure 5). This observation can be explained by the suggestion that the residence time of particles inside the cell is too short in comparison with time needed for formation of 'fibers' in the electric field.

3. Formation and growth of particles in absence of electric field

We now analyze the character of the growth of fractal aggregates within the framework of the diffusion mechanism of aggregate growth based on experimental conditions and data. The first stage of these processes is combustion of methane with an admixture of silicon-contained molecules in air, and this stage proceeds in a hot region of the flame. As a result, particles of SiO_2 are formed, and these particles become solid in a cold region of the flame. Under conditions of this experiment according to the TEM measurements [10] the formed silica particles at height of 7 cm above the burner deck are fractal structures with an average radius of primary particles $r = 8$ nm, an gyration radius $R = 50$ nm and a fractal dimension $D = 1.6$. Based on the velocity of the combustion products $v = 150$ cm/s we estimate the time of this stage of particle growth as $t = 7/150 \sim 5 \times 10^{-2}$ s.

We first consider the mechanism of association of neutral particles and structures which have diffusion motion in a space, so that a contact of two particles or aggregates leads to their association. Then the rate constant k_{as} of association of two particles is given by the Smoluchowski formula [11]

$$k_{as} = 4\pi(D_1 + D_2)(r_1 + r_2), \quad (1)$$

where D_1, D_2 are the gas diffusion coefficients for associating particles with radius r_1 and r_2, respectively. Let us consider the case of association of two particles of radius $r = 8$ nm. The diffusion coefficient D of the particle of radius $r = 8$ nm in air at atmospheric pressure according to the Chapman–Enskog formula [12] is equal ~ 0.02 cm^2/s that results in $k_{as} \sim 10^{-6}$ cm^3/s for two primary particles. To find number density of particles N_p we use the following relation:

$$N_p = 3x_{SiO_2} \cdot M_{SiO_2}/(4\pi r^3 \rho N_{Av})N_M \quad (2)$$