EXPERIMENTAL STUDY ON THE FORMATION OF SILICA PARTICLES IN A COUNTERFLOW DIFFUSION FLAME

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ABSTRACT

We describe a study on the formation of silica particles in a counterflow diffusion flame. This flame is generated in the impingement region of a fuel (H_2+N_2) and an oxidant (O_2+N_2) gas streams. SiH_4 was used as the precursor for the formation of SiO_2. It was fed into the fuel gas stream. Chemical reaction leading to the formation of SiO_2, nucleation of particles, and their initial growth all occur upstream of the flame. For a sufficiently high temperature flame, aggregates formed upstream fuse to form single, spherical particles as they pass through the flame zone. However, for a low temperature flame, aggregates remain (or partially fuse) as they pass through the flame zone. Samples of particles were collected at the exits of the burner. Particle size, shape, crystalline structure, and chemical composition were analyzed. These results will be presented.

INTRODUCTION

The formation of particles in combustion is a problem of considerable importance in many industrial processes. In coal combustion and gasification processes, formation of particles creates a serious problem of air pollution. On the other hand, formation of particles in combustion flames provides a useful technology for the manufacture of many oxide powders.

In the manufacture of powders using flame technology, the formation of particles involves the following processes: (1) The vapor of the desired material (e.g., SiO_2) is generated in the flame by oxidation of the precursor compounds (e.g., SiH_4) which is fed into the flame. (2) The vapor (in a supersaturated state) nucleates and forms initial particles. (3) The initial particles grow to form the desired powder. Since these processes all occur in the flame, the properties of the powder are greatly influenced by the structure of the flame. The structure of the flame is in term determined by the construction of the burner. The design of the burner is therefore a key element in the flame technology for the synthesis of powders.

In our laboratory, we use the counterflow diffusion flame burner designed by Shyan-Lung Chung and Joseph L. Katz [1,2] to study the formation of SiO_2 particles. A main purpose of the research is to investigate the influence of the burner design and the operating conditions (e.g., temperature, concentration, and gas flow paths) on the properties of the particles.

DESCRIPTION OF EXPERIMENT

A. Burner, Gases and Flame

As shown in Fig. 1, the burner consists of two vertically opposed tubes of rectangular cross section. The oxidant (O_2 diluted with N_2) flows downward from the upper tube, and the fuel (H_2 diluted with N_2)

flows upward from the lower tube. The two gas streams meet near the middle and then flow outward. Each tube contains three channels (separated by 0.08 mm thickness stainless steel plates): a central main channel (12.70 mm × 63.50 mm) and two side channels (12.70 mm × 6.35 mm). Fused silica plates, fitted to the outside of the two side channels, force the combustion gases to flow out along the long sides. Each of the burner tubes was designed to obtain a uniform flow of gas across its mouth by passage of the gases through a perforated plate, a bed of glass beads (1.0 mm diameter), and two stainless steel wire screens. To compensate for heat losses from the sides with fused silica windows, the oxidant and fuel streams in the side channels are enriched in O_2 and H_2, respectively, to precisely the extent required to obtain a temperature distribution which is uniform in the direction normal to the two fused silica windows (i.e., the X-direction; the X, Y, and Z directions are shown in Fig. 1). To prevent deposition of particles on the fused silica windows, no precursor compounds (i.e., SiH_4 in this research) is added to the mixtures which are fed to the side channels. Flanges fitted on each side of the burner openings minimize entrainment of surrounding air and keep the outward gas flow parallel to the burner surfaces. The distance between the two burner mouths is adjustable but has been kept at 15 mm in all the experiments presented here.

The major part of the construction of the burner as described above is the same as that designed by Chung and Katz [1,2]. However, in order to study the formation of particles, we have made some modifications. First, the main channel for the fuel gas stream was divided into three slots in the Y direction using 0.2 mm thickness stainless steel plates. Silane can be added to either the central slot or the side slots to study the effect of different flow paths on the properties of the generated particles. (Note that the dividing plates are removable. In some of the experiments, the undivided channel was used.) Second, nitrogen was added to the combustion gases at the burner exits through ten small holes on each flange. This is both to dilute the particles and to quench the effluent combustion gases so that growth of particles can be ceased at the burner exits where samples of particles are taken.

The N_2, H_2, and O_2 gases used all have the reported purities of 99%. A mixture of 10% semiconductor grade silane and 90% U.H.P. grade H_2 (99.999% purity) was used as the silane source. Each gas flows through a filter (sintered brass filter with 0.5 μm pore size) for the removal of preexisting particles. The gas flow rates were controlled and measured to about 1% accuracy using calibrated rotameters.

The burner produces a flame which is flat, stable, and rectangular in shape [1,2]. Both temperature and concentration distributions are uniform in the horizontal plane (i.e., X-Y plane) [2]. Formation of condensing species (e.g., SiO_2), nucleation of particles and their initial growth all occur upstream of the flame, where the gas flow is almost one-dimensional (i.e., Z direction). These characteristics of the flame offer great advantages for the study of the formation of particles.

B. Temperature Measurement

We used 0.05 mm diameter platinum and platinum -10% rhodium thermocouples to measure temperatures. The thermocouple wires were coated with silica to eliminate catalytic effect. The temperatures thus obtained were corrected for radiation loss.

C. Sampling and Analysis

Particles were collected at the burner exits using glass fiber

filters. The crystalline structure of the powder was examined using an X-ray diffractometer (XRD). The chemical composition was analyzed using an energy dispersive spectrometer (EDS). Particle size and shape were examined using an transmission electron micrograph (TEM). To prepare samples for TEM examinations, particles were dispersed ultrasonically in ethyl alcohol. A drop of this dispersion was placed on the TEM grid, and allowed it to dry.

RESULTS AND DISCUSSION

We describe the results of three experiments in the following. These three experiments were carried out using the same H_2-O_2 flame, i.e., the gas flow rates, and the concentrations of hydrogen and oxygen were all kept constant. The gas flow rates are listed in Table 1. In experiment one, the main channel for the fuel gas stream was not divided. In experiment two and three, this channel was equally divided into three slots. Since the dividing plates are very thin (0.1 mm), their effect on the flame is small.

Table 1.

	Fuel		Oxidizer		
	H_2	N_2	O_2	N_2	
Main channel	2260	1270	1600	1210	(cm^3/min)
Side channel	700	0	525	0	(cm^3/min)

In experiment one, the silane flow rate was 20 cm^3/min, which was equal to 0.56% of the total fuel gases. In experiment two, silane was added only to the two side slots. Its flow rate was 13.3 cm^3/min. In experiment three, silane was added only to the central slot at a flow rate of 6.7 cm^3/min. (Note that the silane concentrations in these two experiments were the same as that used in experiment one, i.e., 0.56% of the fuel gases.) The flow rate of the nitrogen used for quenching at the burner exits was 2200 cm^3/min, which decreased the temperature of the effluent gases by about 200°C.

Because the Pt and Pt-10% Rh thermocouples can not measure temperatures above 2000 K, our temperature measurement was limited to the regions outside the flame zone, where the temperatures were below 2000 K. As mentioned previously, the major construction of the burner is the same as that used by Chung and Katz [1]. The gas flow rates, and the concentrations of hydrogen and oxygen we used were also the same as those reported by Chung and Katz in one of their experiments[1,2]. We compared our thermocouple temperature measurements with theirs and found them to be in excellent agreement. We reproduced their temperature profile and showed it in figure 2.

A. Experiment One

Examination of the SiO_2powder collected in this experiment using an XRD shows that it is amorphous in structure. Composition analysis by EDS indicates that the powder is composed of 99.6% SiO_2 and 0.4% SnO_2. In preparing samples for EDS analysis, the powder was fixed on the supporting aluminum blocks using glue containing silver . Since Ag and Sn have overlapped signals, the signal attributed to Sn may be from Ag. Further analysis is required to resolve this confusion.

Figure 3 shows three TEM micrographs of the powder. The powder can be divided into two typesof particles. One is aggregates of very small particles, which are approximately 0.02 μm in diameter. The other is composed of larger, spherical particles whose diameters are approximately 0.1 μm. Some of these particles form aggregates (typically two to five together). However, some of them exist as

single particles. (It should be noted that single,spherical particles have not been found in the published studies on the formation of silica particles, using premixed flames [3,4].)

As illustrated in Fig. 4, we proposed a growth mechanism for the formation of the two types of silica particles in the counterflow diffusion flame. As the fuel gases flow out of the lower part of the burner, silane is oxidized to generate SiO_2 vapor. The SiO_2 vapor (in a supersaturated state) then nucleates and a large number of small particles are produced. These initially formed particles can grow by either vapor deposition or aggregation, or both. In the central part of the fuel gas stream, particles flow through the high-temperature flame zone. The previously formed aggregates fuse to form spherical particles as they pass through the flame zone. This process (as indicated by mechanism (a) in Fig. 4) may explain the formation of the larger, spherical particles found in this experiment. In the outer part of the fuel stream, particles do not pass through the high-temperature flame zone. The previously formed aggregates do not fuse to form spherical particles but remain as aggregates. Further formation of aggregates (or agglomerates) may occur due to interparticle collisions as the particles flow out of the burner. This process (as indicated by mechanism (b) in Fig. 4) may explain the formation of the aggregates of small particles found in this experiment.

B. Experiment Two

The TEM micrographs of the particles collected in this experiment show that all the particles are aggregates of small particles (approximately 0.02 μm in diameter) and that there is no larger, spherical particles. (see Fig. 5) Since silane was added to the side slots, particles may form by mechanism (b) as shown in Fig.4. (Therefore, all the particles are aggregates and no larger, spherical particles are formed.)

C. Experiment Three

The particles collected in this experiment also consist of two types of morphology as found in experiment one. However, there are more larger, spherical particles and less aggregates of small particles as compared with those obtained in experiment one. (See the TEM micrographs in Fig. 6) Since silane was added to the central slot, most particles may form by mechanism (a), thus leading to the formation of more larger, spherical particles. However, some particles in the outer part of the stream may form by mechanism (b), thus leading to the formation of aggregates.

CONCLUSION

Some conclusions may be drawn from the experiments described above: (1) high purity and submicron silica particles can be generated using the counterflow diffusion flame burner; (2) the original form of the burner produces two types of particles; (3) our modification of the burner offers the possibility for the control of the morphology of the particles; (4) the proposed mechanism seems to explain the formation of silica particles in the flame.

ACKNOWLEDGEMENT

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REFERENCES

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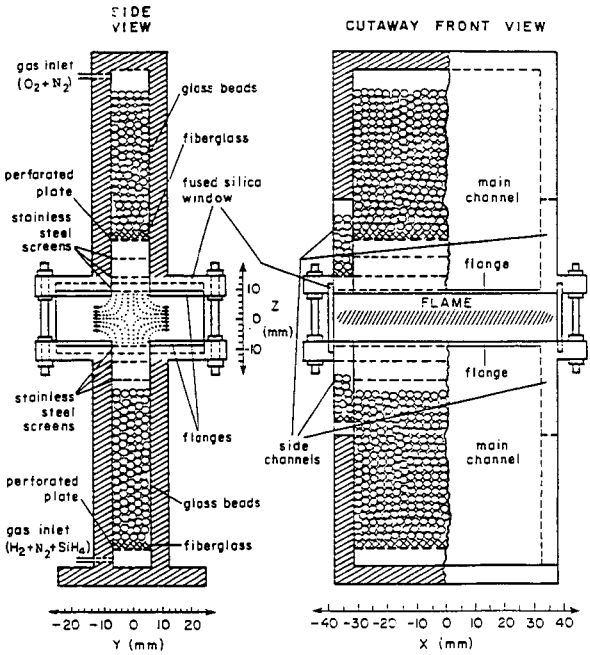


Fig. 1 The counter flow diffusion flame burner.

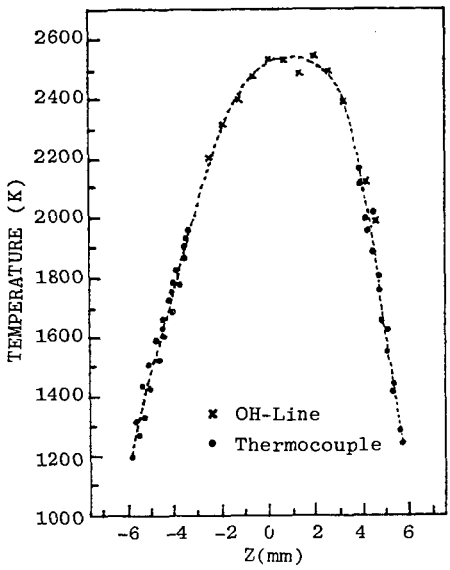


Fig. 2 Temperature distribution along the vertical direction in the counterflow diffusion flame.

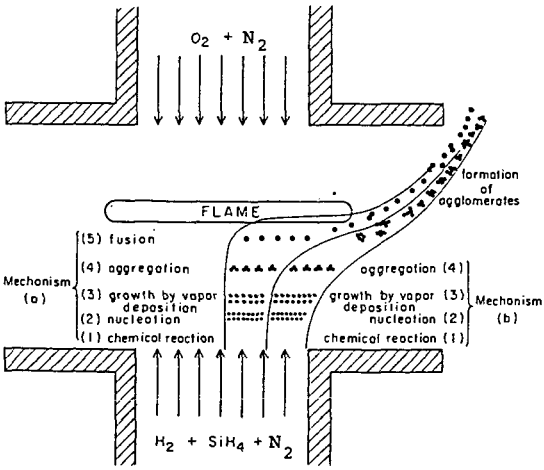
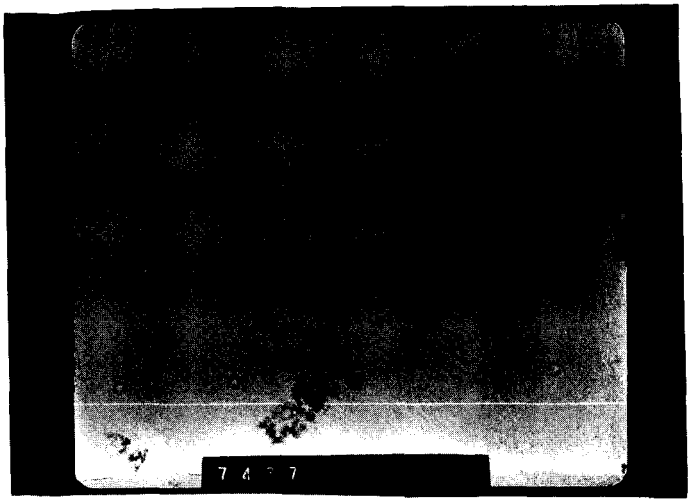
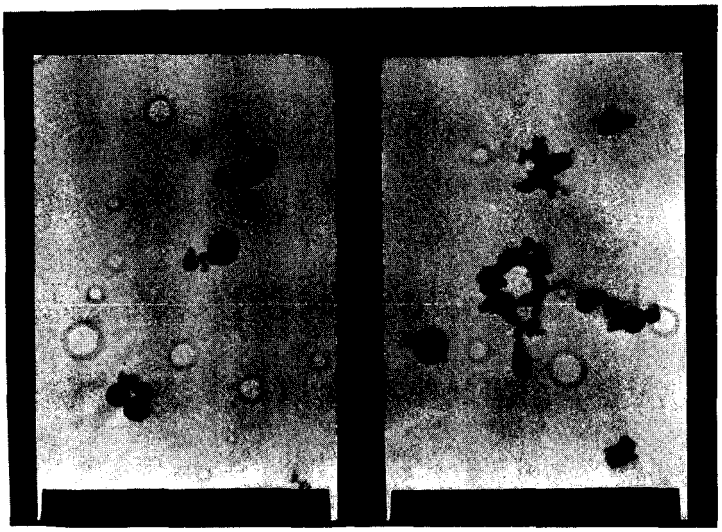


Fig. 4 The particle formation mechanisms in the counterflow diffusion flame.



(a) 24,000×
(0.4 μm)



(b) 30,000×
(0.3 μm)

Fig. 3 TEM photographs of SiO_2 sample.

Fig. 5 TEM photograph of SiO_2 sample.
21,000× (0.4 μm)

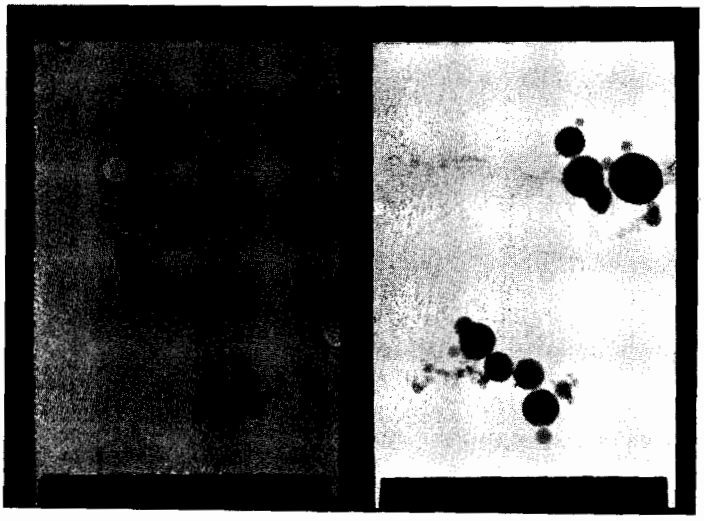


Fig. 6 TEM photographs of SiO_2 sample.
48,000× (0.2 μm)