

Formation of Nanoparticles in Flames Measurement by Particle Mass Spectrometry and Numerical Simulation

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1. Introduction

Combustion processes are the major tool and source of nano sized particles, which sometimes originate as unwanted and even hazardous by-products from industrial or domestic combustion processes. On contrary these nano particles are also produced as useful products in large amounts by combustive and/or pyrolytic methods. Within this frame, the inhibition of particle formation may be desired in order to avoid uncontrolled emissions, while in other cases particular particle quality standards may be required for certain applications. In either case, particle sizing is a necessary tool to investigate and understand the kinetics of particle formation and to provide means of process control. In this study we report on the development of a particle mass spectrometer for the size range of 0,3 to 50 nm and the formation of soot and iron oxide particles in acetylene/oxygen flames. Model calculations were performed for the formation of iron oxide and silicon dioxide in hydrogen/oxygen flames and compared with experimental results.



Fig. 1: Particle Mass Spectrometer attached on top of low pressure burner chamber.

2. Particle Mass Spectrometer

Mass spectrometry for particle sizing has recently been developed by several groups (Gard et.al, 1997; Jayne et.al ; 2000;) to detect particles in exhaust and the environment. Commercially available systems cover the size range of 40 up to several 1000 nanometers. Some of these instruments provide simultaneous size- and composition information of the sampled particles, which requires rather sophisticated setups for sampling and detection. Ziemann and co-workers (1995) developed an aerodynamic lens and an electron beam

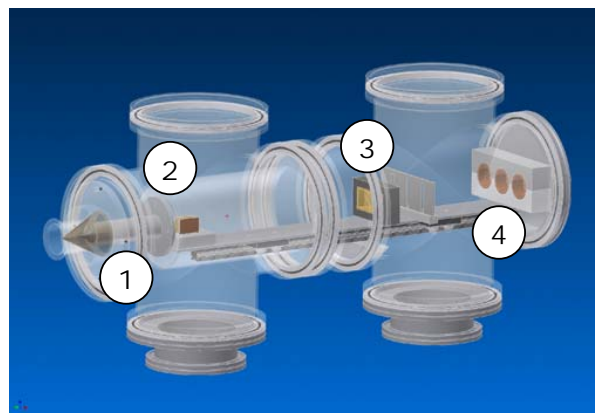


Fig. 2: Schematic view of the instruments components (1) 2-stage molecular beam sampling; (2) deflection plates; (3) measuring of the velocity; (4) Faraday-Cups

charging system to detect uncharged particles in air in the range of 50 to 250 nm.

The particle mass spectrometer (PMS) used in this study has a similar setup as originally described by Hospital and Roth (1990), who reported the measurement of primary particles in flames. It is equipped with a two-stage molecular beam sampling system so that chemical and physical interactions are rapidly quenched and, in particular, all particle – gas interactions are minimized in the measurement system. The incoming particles pass an electric field and the charged fraction of particles is separated according to the sign of charge. The particles are deflected from the straight flight path and collected at Faraday cups. According to the well known TOF-MS principle, the m/z spectrum is determined. The applicable size range of the PMS is 0.3 to 50 nm for singly charged particles. In case of spheres, the particle diameter can then be calculated from the measured particle mass and the known material density (for soot, $\rho \approx 2 \text{ g/cm}^3$; for iron oxide, $\rho \approx 3.9 \text{ g/cm}^3$). The PMS has been constructed to permit sampling from environments with number concentrations higher than 10^9 cm^{-3} without dilution. This makes it particularly suitable for the investigation and control of combustion generated nano-particles. Fig. 1 shows the PMS attached to the burner chamber. A 3-dimensional view of the instruments components is shown in Fig.2.

3. Model Calculations

Model calculations have been performed for the combustion and particle formation from iron pentacarbonyl and silane in premixed hydrogen/oxygen flames using kinetic proposals from the literature (e.g. Rumminger et al., 1999; Lindackers et al., 1997). The mechanisms proposed there have been extended a little to give Fe_2O_3 and SiO_2 as sole final products, and a simple mono-disperse particle coagulation scheme has been added to calculate the time history of the particle number concentration and the particle size. The smallest particle nuclei were estimated to have a diameter of 1 nm, which roughly corresponds to units of ten monomers.

4. Soot Formation in Acetylene/Oxygen Flames

The formation of electrically charged soot particles was investigated in laminar pre-mixed acetylene/oxygen flames burning at 30 mbar. The size distribution of positively and negatively charged soot particles was measured as function of the height above burner and as function of the initial C/O ratio. With the assumption of singly charged particles, double and triple peaks show up in the size distribution (Fig. 3). This feature is known to be unique for soot particles (e.g. Roth and Hospital, 1992), but the reason is not yet clear. Also, it can be seen from Fig. 3 that positive and negative charges are not balanced. Moreover, the charge balance varies with C/O ratio. This indicates a coupling between particulate and gas phase ions, which may depend on temperature. Fig. 4 shows a continuous growth of the soot particles with increasing height above burner.

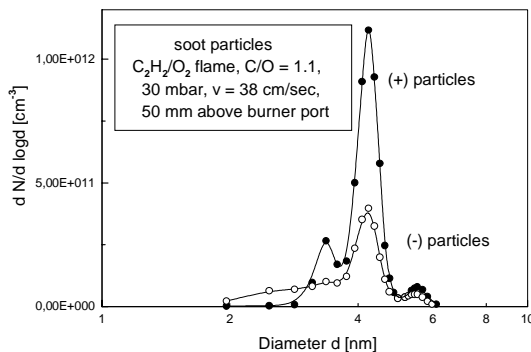


Fig. 3: Size distribution of charged soot particles in acetylene/oxygen flames

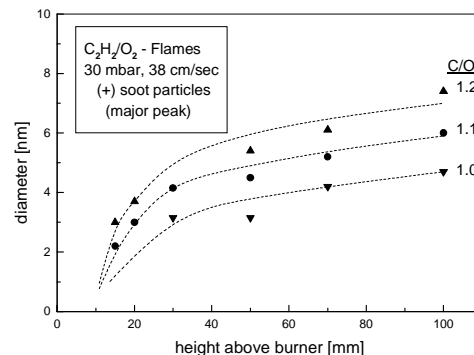


Fig.4: Growth of charged soot particles in acetylene/oxygen flames

5. Iron Oxide in Acetylene/Oxygen Flames

Nanoparticles of iron oxide were produced by adding iron pentacarbonyl (~ 2000 ppm) into the premixed gas of a non-sooting acetylene/oxygen flame ($C/O = 0.42$). Particles could be detected only in the late post flame gases, from a height above the burner of 100 mm and higher. Fig. 5 shows an example of the measured size distributions and Fig. 6 shows the particle growth along the height above burner. Negatively charged particles appear to be formed preferentially in these flames. In comparison to soot formation, the formation of iron oxide particles is clearly delayed.

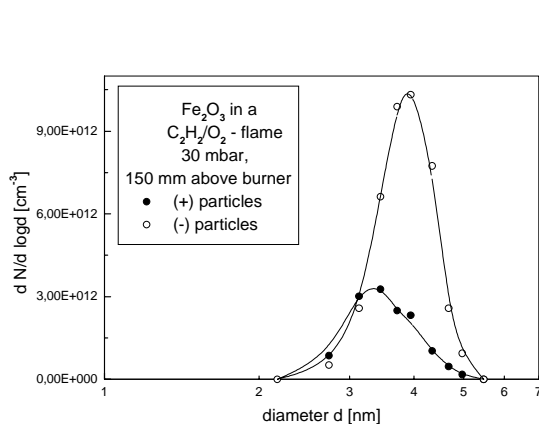


Fig. 5: Size distribution of iron oxide particles in premixed acetylene/oxygen flames

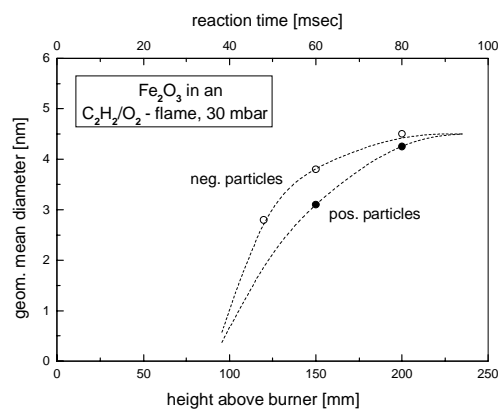


Fig. 6: Growth of iron oxide particles in premixed acetylene/oxygen flames

6. Modeling Results

The formation of iron oxide particles from iron pentacarbonyl and the formation of silicon dioxide particles from silane were modeled for hydrogen/oxygen flames (50 % stoichiometric) burning at 1800 K, i.e. at a temperature similar to those in acetylene/ oxygen flames. As final result, Fig. 7 shows the calculated particle number concentrations and particle diameters as function of reaction time and of height above the burner.

Obviously, the formation of SiO_2 is much faster than the formation of Fe_2O_3 . This is, because iron pentacarbonyl primarily decomposes to form atomic iron which is oxidized comparatively slowly. In the silane chemistry, no such hindrance exists. Fig. 7 also shows that SiO_2 forms larger particles than Fe_2O_3 because of the difference in material density.

7. Conclusions

The formation of soot particles and of iron oxide particles in acetylene/oxygen flames was investigated with a newly developed particle mass spectrometer (PMS). It was shown that the particles have diameters between 2 and 10 nm and grow continuously with increasing height above the burner. In the particulate phase, the charge balance is not complete, hence there is a coupling with the gas phase. Soot ions can be detected very early in the flame gases, while iron oxide particles appear much later in the post flame gases.

Model calculations have been performed for the combustion of trace amounts of iron pentacarbonyl and silane in hydrogen/oxygen flames. It could be shown that iron particles

form more slowly than silicon dioxide particles. In acetylene/oxygen flames, the situation is expected to be similar and therefore, iron oxide is detected only in the late post flame gases.

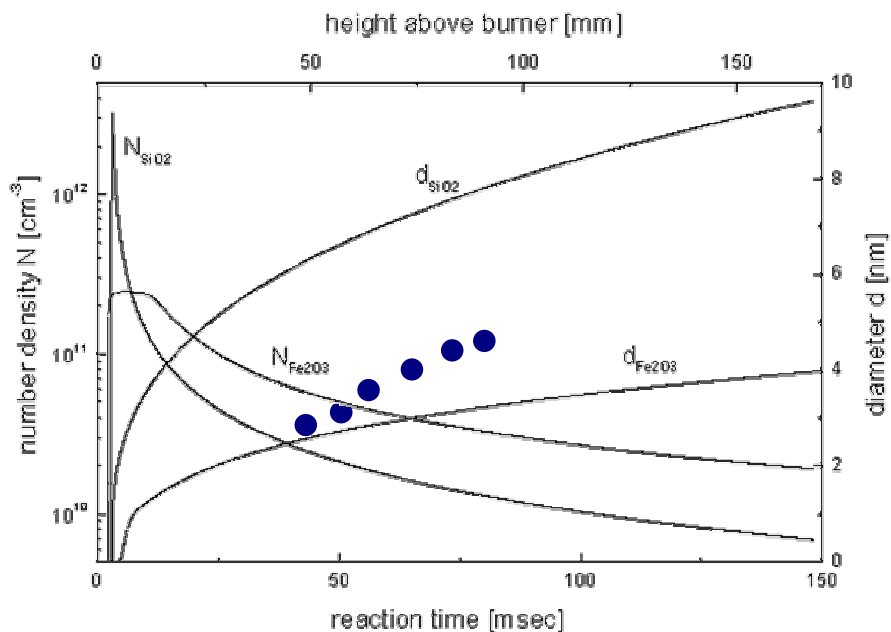


Fig. 7: Calculated formation of nano-particles (iron oxide, silicon oxide) in hydrogen/oxygen flames; Experimental data for iron-oxide nano-particles (●) from Janzen and Roth (2001)

8. References

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