**Lec4**

**SPRAY COMBUSTION METHODS Nanoparticle Production by Flame Spray Pyrolysis:**

In Flame Spray Pyrolysis (FSP), called also liquid flame spray (LFS), a precursor containing a salt of a desired compound is dissolved in a combustible solvent such as ethanol and is sprayed and ignited to form a burning spray flame. The heat generated by the combustion of the fuel and the precursor results in complete evaporation and burning of the solvent and the solid content of the precursor [26]. FSP has high potential for synthesis of composite nanoparticles that can be used as catalysts, sensors and electroceramics.

Typical products synthesized by FSP are TiO2 [27], Al2O3 [28], MgAl2O4 [29], Fe2O3 [30], etc. Multicomponent oxide powders, such as beta-SrMnO3 and NiMn2O4 [31], superconductors [32], and BaTiO3 [33] have been prepared by flame spray pyrolysis of solutions containing inorganic precursors. Production of composite mixed-metal oxide powders with rates up to 250 g/h has been reported [34, 35]. A typical set-up for nanoparticle synthesis by flame spray pyrolysis consists of a spray nozzle, a heat source for initial droplet evaporation and ignition, and an oxidant such as oxygen or air to facilitate combustion.

The nozzle feed rate and spray characteristics, flow rate and type of the oxidant, precursor combustion enthalpy and precursor water content are the parameters that control the temperature and gas phase

reactions of the precursor followed by subsequent particle growth and sintering, taking place within and after the spray flame. The product powder is usually collected by filtration. Micron-sized liquid droplets can be generated, using various atomizers, such as gas-assisted atomizers, ultrasonic atomizers, etc. Controlled synthesis of particles is of great importance in FSP, as a small variation in the processing conditions may alter the quality and properties of the prepared particles.

Spray and flame characteristics and gas phase reactions and processes, such as particle nucleation, coagulation, agglomeration and sintering determine the quality of the powder [36]. While most of ceramic powders synthesized by FSP are made of dense and solid nanoparticles (e.g. [37, 38]), in some cases it has been found that the ceramic powders were an inhomogeneous mixture of large (~ 1μm) hollow and solid dense nanoparticles (~ 10 nm) (e.g. [39- 41]).

The possible mechanism through which an inhomogeneous mixture of hollow microparticles and solid nanoparticles form is illustrated in Fig. (**6**). [36]. Those droplets that entirely evaporate in the hot flame are responsible for the production of nanoparticles: The vapor species react, forming intermediate and product molecules and clusters that quickly grow to nano-sized particles. These primary particles continue to grow by coagulation and sintering, finally forming agglomerates or even hard bonds before being deposited onto the particle collector. On the other hand, under certain conditions, a small number of droplets particularly those with large initial sizes may escape from the spray boundaries and become extinguished to simply produce large hollow or solid particles.



**Fig. (6).** Proposed mechanism of particle formation by flame spray pyrolysis [36].

It is also possible that some of the large droplets that are present in the relatively cool spray core do not completely evaporate. These survived droplets may form large particles that are usually hollow, owing to the high temperature of the process, and may disrupt due to the continuous evaporation of the trapped liquid and pressure buildup inside the hollow particles [4]. Stark *et al.* [42], patented a flame spray pyrolysis process for the production of metal oxides, particularly ceria, and ceria/zirconia catalyst particles that have a monolithic structure.

Another part of their patent concerns the addition of ceria or yttria to stabilize zirconia to make it suitable for application in fuel cells and sensors. In their patent, the novelty is the method of producing the precursor solution, which is claimed to result in good mixing at atomic level in production of mixed oxides: One metal precursor is dissolved in a high enthalpy solvent comprising at least one carboxylic acid with a mean carbon content of greater than 2 carbon atoms in an amount of at least 60% of total solvent to form a solution. They also placed some restrictions on the minimum required enthalpy of the solution that would lead to the formation of a homogenous mixture of the nanoparticles. The rest of the process is more or less similar to the general flame spray pyrolysis process described above.

Another version of the flame spray pyrolysis, called liquid-fed flame spray pyrolysis (LF-FSP) was patented by Laine *et al.* [43], In this process, pre-formed particles are injected into the high temperature zone (flame) along with the liquid precursor of the same or a different composition. As a result of this process, the resulting particles may be different in composition or morphology. As an interesting scenario, the pre-formed particles may become coated with solid derived from the liquid precursor.

The initial particles may be natural or synthetic with sizes from several nanometers to 100 micrometers.

The concentration or number density of the initial particles suspended in the precursor solution should be such that the atomization of the precursor is not interrupted. By controlling the flame temperature, the desired morphology or composition of particles are achieved.

The flame may be produced by oxyhydrogen torch or by combustion of liquid or gaseous fuels. As an example, they used 1 wt % suspension of 􀀂-alumina with particle sizes smaller than 20 nm in liquid EtOH/ButOH 50/50 vol%.

The resulting powder was a mixture of 􀀁- and 􀀃-alumina particles. Kodas *et al.* [44], patented an FSP process similar towhat that was explained earlier, except they state that in their invention the process typically occurs in an enclosed flame spray reactor. The process consists of providing a precursor medium comprising a liquid vehicle and a precursor to a component, flame spraying the precursor under conditions where nanoparticles are formed.

However, they did not elaborate on these conditions. In their patent, they emphasized on the percentage of the final particles that may be nano-sized. For instance, in one aspect, they state that greater than about 90 percent by weight of the precursor to the component in the precursor medium may be converted to the component in the nanoparticles. This implies that in this process an inhomogeneous mixture of nano- and microparticles are formed. This is in contrast to the patent by Stark *et al.* [42], where the invention is based on the selection of high enthalpy solvents so as to produce homogeneous nanoparticles.

As an example, Kodas *et al.* [44] reported the production of aluminum doped zinc oxide particles with

applications in the manufacturing of solar cells and displays. The solution is prepared by mixing aluminum diisopropoxide ethylacetoacetate, zinc 2-ethylhexanoate and toluene. The weight percentage of aluminum and zinc in the precursor solution is 0.2 and 5.6, respectively. Their SEM and TEM analyses showed that the particles were crystalline and partially agglomerated with a size range from 40 to 150 nm.

A process for the production of phosphorescent oxide nanoparticles with rare earth element dopants, again in the category of FSP, was patented by Ju and Qin [45]. In their patented process, the precursor solution is polar and could be aqueous or non-aqueous; the solution is converted into droplets and droplets are carried to a chamber where they become suspended in a surrounding inert gas. The suspended droplets and the carrier gas are contacted with a flame fueled by reactive gases, where the droplets are heated in the flame to a temperature sufficient for a chemical reaction to occur Fig. (**7**). The main difference between this invention and the conventional FSP method is in the manner the flame is produced and sustained.

In the former, the flame is separately produced by a gaseous fuel, whereas in the latter the precursor solution can form a self-sustained burning spray flame. As an example, ultrasonic atomization was employed to produce a fine spray of droplets carried to a chamber by nitrogen gas through a 5.3 mm pipe. The flame was fueled by oxygen and methane. Similar to other FSP processes, the particles were collected on a filter downstream of the flame. A process to produce and functionalize nanoparticles was patented by Guo *et al.* [46],