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Synthesis of Nanoparticles through Flame Spray Pyrolysis: Experimental Apparatus and Preliminary Results

Giulio Solero

Politecnico di Milano, Campus Bovisa, Dipartimento di Energia, Milano, Italy

Abstract Nanostructured materials represent nowadays a wide, and probably still largely unexplored, field of potential applications. In fact, this is a research topic in high and rapid development, both at a basic level and under the point of view of possible practical applications, leaving large space for a thorough scientific analysis, which requires with no doubt long time for ultimate conclusions. This paper deals with the preliminary work performed in the field of FSP (Flame Spray Pyrolysis) synthesis for nanoparticles, using an external mixing gas assisted nozzle. Particularly, an experimental apparatus has been designed, realized and characterized for the controlled synthesis of nanoparticles by the flame spray pyrolysis technique. The apparatus consists of a gas-assisted spray for droplet generation and dispersion in a secondary pilot flame. By dissolving suitable precursors in a liquid fuel, different types of nanoparticles have been produced. In the preliminary tests SiO_2 and TiO_2 have been synthesized and characterized by TEM analysis and XRD, respectively, as a function of the main operating conditions (for instance, precursor concentration) of the experimental apparatus. The designed set-up shows good stability and reproducibility of the reaction flame and, therefore, of the material produced and the obtained results, even if preliminary, encourage the use of the experimental apparatus for the controlled synthesis of nanostructured materials.

Keywords Nanomaterials synthesis, Flame spray pyrolysis, Combustion

1. Introduction

Nanostructured materials represent nowadays a wide, and probably still largely unexplored, field of potential applications. In fact, this is a research topic in high and rapid development, both at a basic level and under the point of view of possible practical applications, leaving large space for a thorough scientific analysis, which requires with no doubt long time for ultimate conclusions.

The potential application fields of nanoparticles are very wide and, probably, not yet fully understood: from energetics (sensors, propulsion, reduction of environmental impact) to chemistry (catalysis, additives) to medicine (diagnostics) and of course to material science. For instance, recent studies [1, 2] put into evidence that inert nano-additives can influence combustion features of Diesel sprays with possible important effects on propulsion systems. In the field of rocket propulsion the use of nanoparticles can enhance the engine performance under the point of view of specific thrust [3]. Also the problem of nanoparticles impact on human health is a rather unexplored field. The same can be said about the study of the different methodologies for controlled synthesis of nanoparticles. In fact, numerous processes are utilized for the synthesis of nanostructured materials and in particular for nanoparticle production. These processes can be divided in three main categories [4]. The mechanical methods obtain a reduction of the particle dimensions through mechanical systems such as the "ball milling" technique. The liquid-chemical methods rely on the precipitation of a solid in a solution or the chemical conversion of colloidal dispersions in a gel ("sol-gel technique"). The high temperature methods for the synthesis are numerous and include evaporation/condensation techniques, aerosol techniques and flame synthesis [5]. The high temperature synthesis offers several advantages for nanoparticle production in terms of both purity of materials and size control of the particles. For the flame synthesis process there are two main ways to inject the precursor in the flame: in homogenous phase, through an evaporation system at controlled temperature, or through a spray system, in liquid phase (FSP: Flame Spray Pyrolysis). This last methodology offers a greater flexibility in terms of type of precursors to be used and flow control determining the amount of produced material.

The advantage of the Flame Spray Pyrolysis technique (FSP) is the use of a wide variety of possible low cost precursors (mainly in the field of metal oxides such as TiO_2, Al_2O_3), obtaining a final product with high purity and relatively narrow size distribution [6, 7]. FSP seems to be a versatile process allowing a strict control of the produced nanomaterial, particularly product size and morphology

* Corresponding author:
giulio.solero@polimi.it (Giulio Solero)
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strictly depend on precursor concentration and dispersion gas flow rate [8, 9]. Moreover, also inorganic nanorods can be synthesized through this technique [10]. A typical experimental set-up [11, 12] is constituted by a unit for droplets generation and dispersion (usually a gas-assisted spray), a heat source for droplets evaporation and ignition and an oxidant for combustion. The simplest way to generate micron size droplets is the use of an assisted atomizer, which presents also optimal features under the point of view of homogeneity of droplets size. Obviously, due to the complexity of the physical and chemical phenomena involved in the controlled synthesis by FSP, investigation should be performed about the influence of the operating conditions of the spray (flow field, dimensional distribution, precursor typology and physical properties, gas to liquid mass ratio, oxidant typology) on the final product, that is on the morphological and structural properties of the derived nanoparticles.

2. The Experimenyal Set-up

This paper deals with the preliminary work performed in the field of FSP synthesis, using an external mixing gas assisted nozzle, presented in Fig. 1.

As it can be observed, the experimental apparatus consists of a spray nozzle containing a capillary tube (0.3 mm inner diameter, 0.8 mm outer diameter) that lies in an opening of 1 mm diameter at the spray top, thus creating an annular gap. The liquid precursor is mixed with a liquid fuel and then the solution flows from a reservoir inside the capillary, while the dispersion gas (air or oxygen) flows inside the annular gap. The capillary ends a little downstream the opening, giving rise to an atmospheric spray flame ignited by a premixed methane-air flame which is concentrically arranged around the nozzle exit. This sustaining flame was kept just slightly rich, thus originating an overventilated cone in the presence of the oxidant [13]. The gas flow rates are measured and controlled by thermal mass flow meters. The apparatus is designed in order to achieve, through the longitudinal displacement of the dispersion gas injector, a variation of the outflow area, from zero to the maximum value. By maintaining constant the exit area, the dispersion gas flow rate depends on the upstream applied pressure till the critical value is achieved. The pressure in the dispersing gas supply chamber was monitored in order to operate always below such critical level.

The combustion gases are conveyed in a hood connected with a vacuum pump in order to collect the produced nanoparticles. The hood is equipped with a filter (Whatman GF/A) 150 mm in diameter, placed rather far away from the flame tip. Thermocouple measurements have been carried out to ascertain that the temperature at the filter level were low enough to avoid changes in the material, e.g. sintering or phase change for crystalline materials. As a general rule, this temperature was kept around 300 ℃.

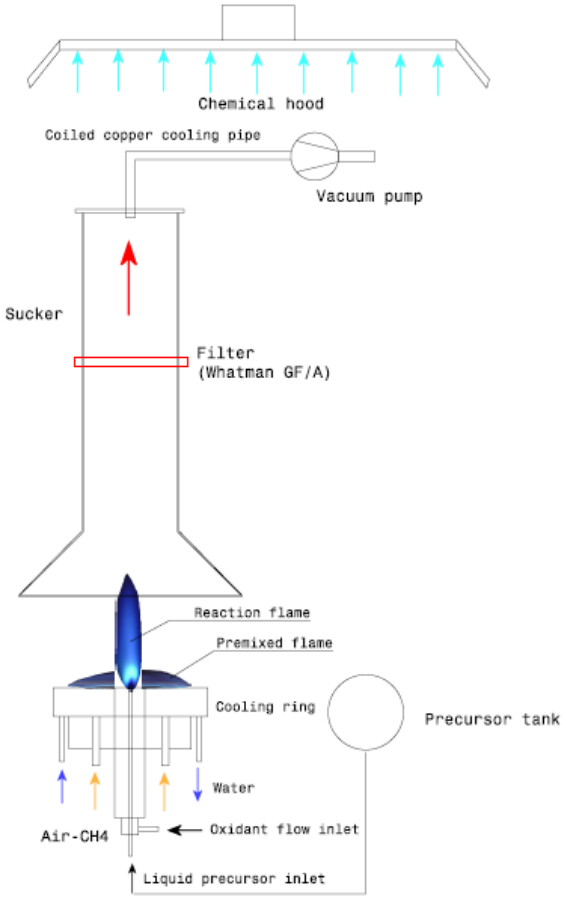

Figure 1. Schematic view of the experimental set-up

3. Experimental Results

As outlined in the Introduction, the main features of the nanoparticles (especially under the point of view of size distribution and morphology) to be synthesized in the combustion process depend on the structure of the spray. It is important to achieve a constant range of droplet size as a function of different operating conditions. In order to investigate the dimensional distribution of the generated droplets as a function of dispersion gas flow rate and gas to liquid mass ratio, the behaviour of the spray jet has been initially characterised in isothermal (cold) conditions, both through visualizations for qualitative analysis and PDA (Phase Doppler Anemometry) for quantitative measurement of mean droplets size.

Figure 2 shows a typical isothermal water spray as obtained by our nozzle. The general morphology of the spray seems quite homogeneous, the big spots are falling droplets after condensation in the ambient air.

Subsequently the spray has been carefully investigated by PDA. For this purpose a Dantec Dynamics phase Doppler anemometry system (based upon the use of an Ar-ion laser as light source) has been used in order to characterise the spray behaviour in cold conditions, providing the mean droplets size.

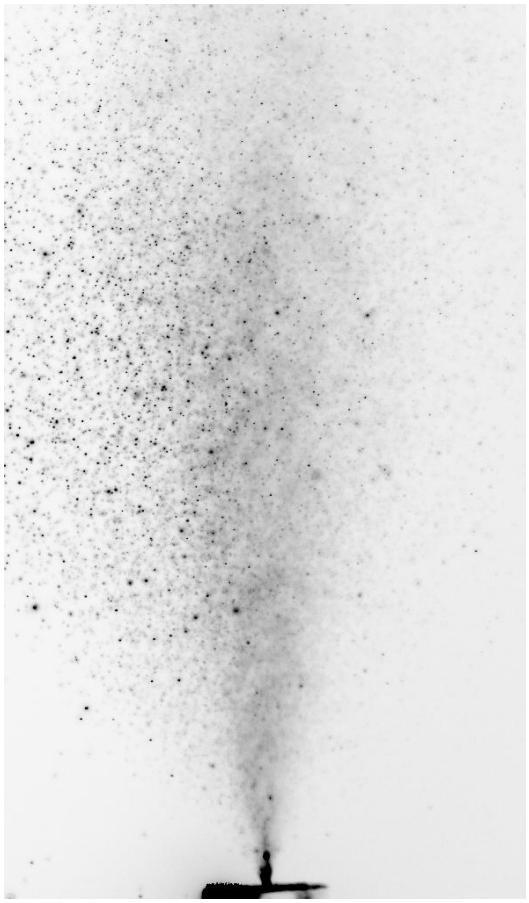

Figure 2. Image of the water spray

Figure 3 shows the comparison of the counter mean diameter (CMD) for the water spray and the n-hexane spray at 5 mm from the burner exit by varying the oxygen flow. For flows of oxygen higher than 4-5 l/min the size of the droplet is almost constant for both liquids. N-hexane fuel produces smaller droplets than water (about 11 μm against 19 μm). The radial profile of CMD was also investigated. As an example fig. 4 shows the CMD radial profile for the water spray at 50 mm from the exit nozzle. The diameter of the droplet is almost constant with a value of about 13 μm.

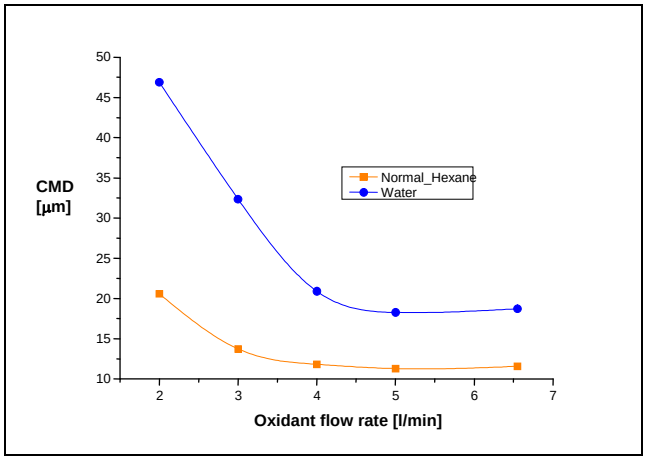

Figure 3. Comparison of the counter mean diameter (CMD) for water and n-hexane spray at 5 mm from the exit nozzle

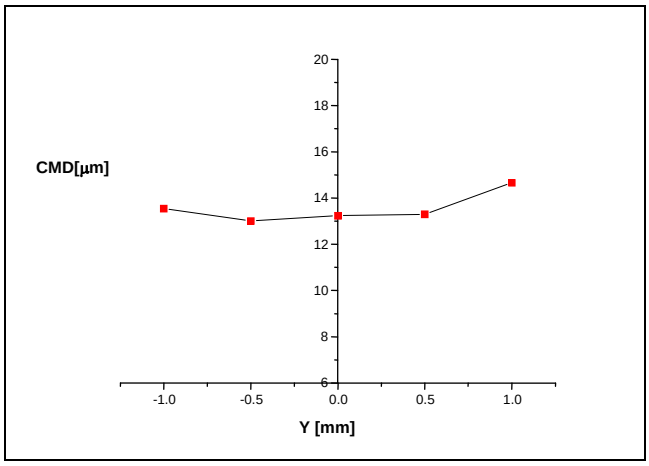

Figure 4. Radial profile of the CMD for the water spray at 50 mm from the exit nozzle

Having identified a suitable operating field (in which the mean droplets size is almost constant), the spray has been ignited using n-hexane as fuel and tetraethoxysilane (TEOS) as liquid precursor, to obtain silica nanoparticles, and oxygen as dispersion-oxidation gas.

Figure 5 shows the blue flame obtained flowing only the liquid fuel, while in fig. 6 the flame exhibits a pink colour due to the TEOS reaction during SiO_2 nanoparticles synthesis. In general the height of the visible flame, using an oxygen flow rate of 4 l/min, is in the order of 8 cm. A layer of powder has been collected on the filter placed in the hood, as previously described. The nanoparticles have been analyzed with a Transmission Electron Microscope (TEM) (Jeol Jem 2000 FXII), allowing a preliminary analysis of the dimensions as a function of the main operating conditions (such as gas flow rate and gas to liquid mass ratio). For TEM analysis, a very small quantity of powder was placed in ethanol and, after sonication, a droplet of the suspension was dried on a TEM grid.

Figure 5. n-hexane spray flame

Figure 6. n-hexane with TEOS precursor spray flame

Figgs. 7-8 show two examples of aggregates of SiO_2 nanoparticles as synthesized in the spray flame. Figure 7 refers to a 0.5 molar solution of TEOS in n-hexane with a liquid flow rate of 1 ml/min. The nanoparticles have a size of about 15 nm and appear to be sintered with necks of comparable size of the particles. This is due to a low concentration of precursor and a high flame temperature. In fig. 8 a different structure is observed. The higher molar concentration and flow rate (1 mol., 3 ml/min) result in the formation of large and round nanoparticles of size up to 40 nm together with smaller particles. This is a rather recurring feature, well predicted by models [14 and references therein]. In fact, higher precursor concentration involves higher collision frequency, thus enhancing the formation of larger particles. Moreover, the intradroplet reactions take place more easily, leading in some cases to the formation of one particle from a whole droplet.

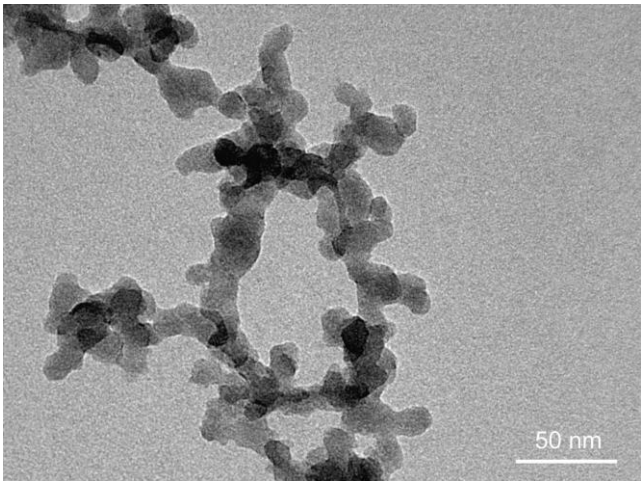

Figure 7. SiO_2 nanoparticles synthesized in the spray flame: 0.5 molar solution of TEOS, 1 ml/min

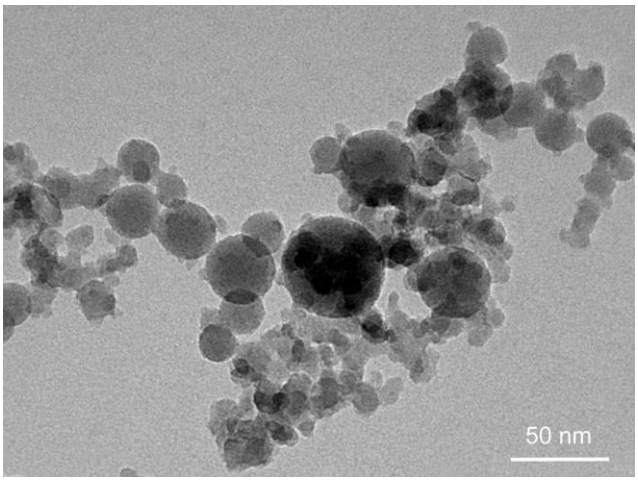

Figure 8. SiO_2 nanoparticles synthesized in the spray flame: 1 molar solution of TEOS, 3 ml/min

The spray flame was also tested for the synthesis of TiO_2 nanoparticles. To this purpose Titanium Tetraisopropoxide (TTIP) was dissolved in ethanol to form a 1 molar solution and with a flow rate of about 1 ml/min. The flame exhibited a brilliant whitish colour and titania nanopowder was collected on the filter. Provided that crystal structure is the most important feature for titania [15], XRD measurements were performed on a thin powder layer deposited on a steel sheet. The result is shown in Fig. 9, where only the major peaks of the resulting spectrum are reported.

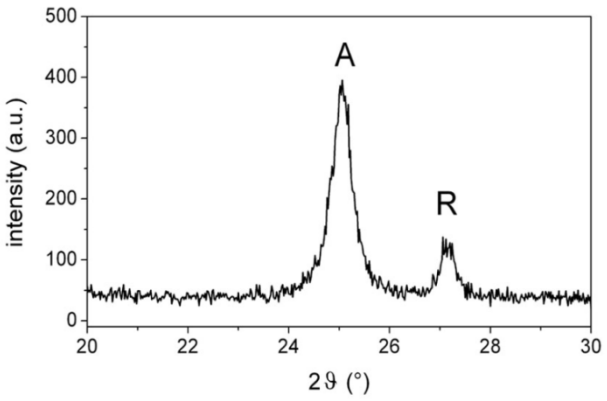

Figure 9. Main peaks of the XRD spectrum of synthesized titania nanoparticles (A = anatase, R = rutile)

As it can be seen, the anatase phase is largely prevailing in the collected powder (86,3% anatase and 13.7% rutile) and this can have positive effects on practical appliances of the synthesised nano-powders. In fact, it is well known [16] that anatase is generally considered as the most active phase for photoelectrochemistry, especially for water splitting, and photocatalysis. From the structure of the peaks it is also possible to derive an estimate of the average crystallite size, that in this case results to be between 15 and 20 nm.

4. Conclusions and Future Work

An experimental apparatus has been designed, realized and characterized for the synthesis of nanoparticles by the flame spray pyrolysis method. The apparatus consists of a gas-assisted spray for droplets generation and dispersion in a secondary pilot flame. By dissolving suitable precursors in a liquid fuel, different types of nanoparticles have been produced. In the preliminary tests SiO_2 and TiO_2 have been synthesized and characterized by TEM analysis and XRD, respectively. The experimental set-up shows good stability and reproducibility of the reaction flame and, therefore, of the material produced. The influence of operating conditions of the synthesis apparatus (mainly, the precursor concentration and flow rate) upon the morphology of the nanostructured material has been preliminarily investigated. The titania nanoparticles generated by the FSP apparatus show (through XRD analysis) a crystal structure (≈86% anatase) suitable for practical appliances in the field of photocatalysis.

The obtained results, even if preliminary, are anyway promising and encourage the use of the designed experimental apparatus for future work in the field of controlled nanomaterials synthesis through FSP. Particularly, further analysis will be devoted to the following aspects:

- sensitivity analysis of the experimental set-up through a detailed study of the influence of the spray operating conditions (for instance: precursor typology and concentration, oxydant and fuel flow rates) upon the structure of the nanomaterials synthesized (TEM and XRD analysis are useful instruments for this purpose);
- improvement of the collection system of the generated nanopowders, for instance by an automatic mechanism: this can provide useful informations about the degree of conversion of the chemical reactions involved in the synthesis process;
- use of the FSP apparatus for the synthesis of other types of nanoparticles, varying the precursor.

Moreover, the results that will be obtained in the near future through the designed experimental set-up can be useful for the tuning and validation of theoretical models about nanomaterials synthesis mechanisms.

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