Perspectives for development and industrial application of spray pyrolysis method

S. Kozhukharov, S. Tchaoushev

Abstract *The production of industrial products is based on the specific combination among applied methods, as well as the conditions of synthesis, (temperature, pressure, rates of gaseous and liquid fluxes). By the other hand, both of the methods and conditions for synthesis depend on the available equipment, which enables the suitable conditions for processing and further treatment of desired product. The entire behaviour of the corresponding products during their exploitation depends on their features, predetermined simultaneously by their form, composition and structure. All these properties are natural consequences of the technology applied, as a combination of methods, conditions and equipment. In this sense, the present work is an attempt to summarize the basic kinds of methods, equipment, and conditions for obtaining of products for various applications..*

Key words: Spray pyrolysis, SPS, SPD, conditions, applications

INTRODUCTION

On the basis of the literature's data, could be considered that the spray pyrolysis (SP) method is based on spraying of liquid solutions various (predominantly metallic) compounds through spaces with controlled high temperatures. The characteristics of the products obtained via this method are entirely predetermined by both of the compositions of the initial precursor's solutions and the conditions applied. The latter depends on the features of the equipment employed in each particular case. By the other hand, the commercial purpose for application of the respective products predetermines the most appropriated compositions of the initial solutions, conditions of synthesis, and the necessary equipment, respectively.

In that means, the aim of the present work is to summarize the correlations among the properties of the products, the conditions of their synthesis, and the features of the respective equipment.

Regarding the form of the obtained product, the spray pyrolysis method could be divided into two General groups: *Spray Pyrolysis Synthesis* (SPS) – for obtaining of powders and *Spray Pyrolysis Deposition* (SPD) – for obtaining of thin films.

Spray Pyrolysis Synthesis (SPS): According to [1], when a liquid drop of solution is already sprayed, it undergoes several processes in the high temperature space, until its conversion to a solid particle. These processes are illustrated in figure 1, and described in brief below:

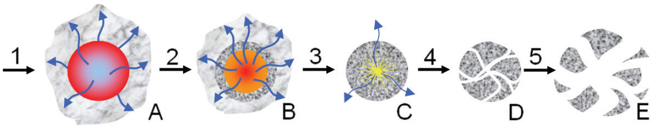

Fig. 1. Thermal processes related to SPS

Initially, each drop suffers heating, and evaporation of the solvent (1), until it achieves the stage A. It could be described as a liquid particle, represented by saturated solution, surrounded by vapors of the solvent. Afterwards, due to the evaporation, an additive solid shell forms (2), leading to intermediated three phases system (B). It is represented by vapors, solid porous shell, and still liquid core. That process passes simultaneously with initiation of chemical conversion of the precursors to the desired product. During this stage, an additive interaction between components of the vapors and the solid shell are possible, as well. By that manner, Kalyana [2] succeeded to obtain partially fluorinated TiO_2 as photocatalyst with improved activity. After completion of the evaporation, because of expense of the entire liquid, a spherical solid particle of the product appears (C). The process could be finished until this stage. That approach is also known as “one drop – one particle”. In that means, some authors [3 – 6] prefer to use ultrasonic nebulizers, in order to decrease the size of the spray drops. It enables production of powder materials with one fraction size of particles. If these particles are submitted to further calcinations, then they could split-up to form even smaller particles (E). That approach permits production of ultra dispersive nano-particles. The transition from stage C to E, passes trough intermediate stage D. This stage could be reached, because of appearance of cracks and ruptures (4). Their appearance is consequence of mechanical tensions, due to difference of the temperatures, and the volume expansions between the core and the surface of the respective particle. Another reason for the crumbling of the particles is that the processes described above could pass accompanied by polymorphic transitions in the solid phase. All of these processes pass in the zones of the evaporator, and the furnace (figure 2, positions 5 and 6, respectively). Both of further calcination and use ultrasound nebulizer enable large scale production of nano-particles.

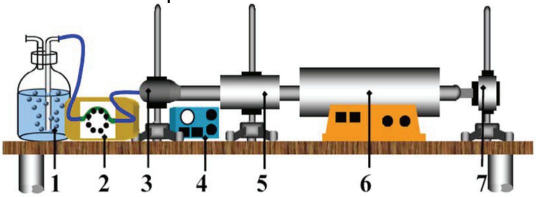

Fig. 2. Schematic view of horizontal SPS equipment

1 – Recipient with precursors solution; 2 – peristáltic pump; 3 – pulverizator; 4 – sistem electric feading; 5 – evaporator; 6 – furnace; 7 – filter and collector for the product.

Large number of examples for employndment of horizontal devices for SPS could be found, [7 – 10], as well as for commercial equipment [11]. There is a variety of devices which could be employed for SPS. The constructions of the chambers for SPS could be divided generally to horizontal, or vertical. Kang et al. [3] have used vertical chamber for obtaining of $NaTaO_3$ as a photocatalyst. Vertical chamber was used by other researchers for obtaining of water splitting ferrites for solar hydrogen production [3]. Here should be mentioned that Hirunlabh et al. [13] noticed the advantages of thermal chamber with horizontal position, which permits simultaneous separation of larger and smaller particle’s fractions. Due to the pressure difference between the nozzle and the bulk of the thermal chamber, the particles endeavor to cross as large distance, as possible. At the same time, the weight of particles causes their falling on the bottom. As result, the horizontal construction renders separation of various fractions of with different size. In addition, a combination of vertical and horizontal constructions is also proposed [8].

Besides the electric resistive heaters, such as kanthal [9 – 11], alternative sources of heat could be also employed. If, the spraying nozzle is substituted by a burner, then the entire spray could pass directly trough a flame [6, 12-14]. Tani [13] defines this kind of SP as Flame Spray Pyrolysis (FSP). Alternatively, electric arc plasma induced SP is also described in the literature [16]. Todorovsky et al. [17] have produced large variety of metal oxides, using spray pyrolysis, combined with Nd:YAG solid laser irradiation and magnetic field.

Spray Pyrolysis Deposition (SPD): The SP method could also be applied for obtaining of various thin films. The thickness of the obtained films is so important for SPD, so the particle’s size of the powders at SPS. It is proportional to the spray flow per given surface area of the substrate, and the duration of its residence in the furnace. Here, should be mentioned, that relatively prolonged residence predetermines more uniform and smooth layers. In addition, SPD enables multilayer systems, by multiple repetition of the spraying. Okuya and co. [18] have successfully created entire multilayer UV sensor by employment of this approach. Afifi and co. [19] propose application of SPD for production of solar cells. Another important characteristic of the films are their density and structure. It could be determined by posterior annealing. Shindov [20], remarks that the high temperature's posterior annealing of SP-deposited CdO leads to formation of larger crystals, with more uniform distribution. Other investigations for usage of laser beam are described by Starbov et al. [21]. They also used excimer laser for posterior annealing of ZnO layers, deposited on lime soda glass substrates. According to the authors, this posterior procedure had improved significantly the properties of the obtained products as gas sensors. Genearlly, the posterior annealing at moderate temperatures, leads to decrease of whatever mechanical tensions between the substrate and the corresponding coating. Such tensions could appear as consequence of the different volume expansion (i.e.: dilatation) coefficients of the respective materials.

The most important parameter for the quality of whatever deposited film is its adhesion to the substrate. In that means, SPD could be performed either directly hot spray, or by cold spray on preliminary heated substrate. In both cases, the adhesion arises as consequence of partial superficial fusion of the substrate. Nascu and Popescu [22] have obtained variety of CdS films with different colour related properties, by varying of: temperature of the substrates (glasses), concentration of the initial solutions, addition of surfactants, etc. Here should be mentioned, that always the optimal temperature of the substrate should be determined by heating microscopy for the respective substrate – film system. The preliminary measurements should be performed as is described in [23]. Taking in account that the SP is a typical high temperature method of synthesis, the behavior of the respective substrate, and material for coating at high temperature should be evaluated. For that reason, high temperature characterizations, as thermogravimetry, (TG), differential thermal analysis (DTA), dilatometry, etc should be employed on both of the substrate, and the corresponding coating material. For these purposes, integral combined analytical devices are commercially available [24].

Conjunction among the product properties, the conditions of synthesis, and available equipment

Having in account the variety of above described methods and approaches for obtaining of different products, could be concluded that the characteristics of the products depend directly on the precursors, as well as the conditions of their synthesis. The latter, by the other hand, is predetermined by the abilities of the available equipment.

Thus, the products of the spray pyrolysis approach should possess properties which correspond to the purpose of their usage (refraction ability, density, photocatalytic ability, ect). The properties, revealed by these products predetermine the available market. By other hand, they are predetermined simultaneously by the precursors, and the conditions for their obtaining. The conditions, by their side, depend on the availabilities and design of the corresponding equipment. In detail, the basic variables, which could be drawn, are as follows:

1-Speed of the flow from the nozzle – it predetermines the size of the drops, and obtained particles. 2-Temperature – It predetermines the intensity of the evaporation of the solvent, and consequently – the porosity of the obtained film/particles. 3-Presence or absence of ultrasound generator; its presence always should predetermine smaller size of the drops, as consequence, either smaller particles, or thinner and smoother films will be obtained. 4-Chemical composition and flow could significantly influence over the size of particles, and the composition of the final product.

It should be concluded that there is clear conjunction among the composition, properties, structure and form of the products. This conjunction predetermine the behaviour of the corresponding product, and by the other hand, they depend strongly on the features of the equipment used. This conjunction is represented in figure 3:

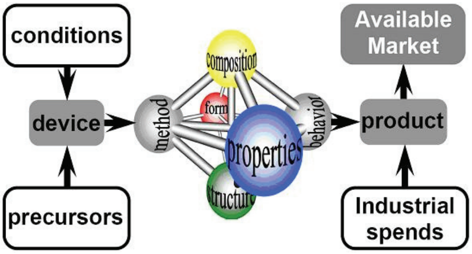

Fig. 3. Conjunction among the features, behaviour and conditions of products, produced by the method of SP.

CONCLUSIONS

There are several basic groups of constructions of equipments for spray pyrolysis:

- According to position of the chamber – horizontal or vertical. The horizontal construction permits size separation of the drops/particles.

According to the heating source - it could be electric heater, laser, direct flame, or even electric arc plasma. The FSP approach requires alimentation of the nozzle, simultaneously by combustible, precursors and oxidant. Alternatively, additive burner should be mounted to the chamber.

In the cases of film depositions, (SPD) the corresponding substrates should be heated. That approach permits cold spraying on preliminary heated substrate with posterior annealing and drying of the obtained film. This approach permits much more fine control over the structure formation during deposition. Posterior annealing of the coated products at moderate temperatures could result to an additive improvement of their quality.

The subsequent repletion of the SPD method permits formation of multilayer systems, which could possess various combinations of properties.

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