



Perspectives of spray pyrolysis for facile synthesis of catalysts and thin films: An introduction and summary of recent directions



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ABSTRACT

In the modern technological world, applications are rapidly demanding homogeneous, reproducible, scalable processes for films and catalytic surfaces. The uses of spray pyrolytic methods for fabricating these films have received attention since the late 1980s, and today spray pyrolysis finds use in a variety of applications, ranging from biomedical to industrial, microelectronics to ceramics. In this review, basic parameters of spray pyrolysis for catalytic and thin film formation are summarized, while recent developments in spray deposition for environmental remediation, photovoltaics, fuel cell and battery materials, biomedical applications, and microelectronics are also discussed.

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1. Introduction

In the modern technological world, applications are rapidly demanding homogeneous, reproducible, scalable processes for films. The uses of spray pyrolytic (SP) methods for fabricating these films have received attention since the late 1980s, though today spray pyrolysis finds use in a variety of applications, ranging from biomedical to industrial, microelectronics to ceramics. A comprehensive review of spray pyrolysis is a difficult task to undertake; we have thus chosen to restrict ourselves to non-plasma methods, focusing on liquid, powder, and flame-spray deposition techniques. There are many other published reviews and we will mention these here that the reader is referred to for further information. We present a comprehensive introduction to spray pyrolytic techniques in liquid and powder form; as well as a summary of current

status of industrial and chemical progress in the field of spray pyrolysis in a variety of disciplines, including photocatalysis, ceramics, and electrocatalysis.

2. Spray pyrolysis parameters

2.1. Atomization of liquids

Spray pyrolysis techniques involve the acceleration of a liquid or liquid/solid phase precursor solution from a specially designed atomizing nozzle (atomizer) to carry a droplet of reagents to a surface or interface. There are various parameters based on which the atomizer are classified. We have based the respective methods on different sources of energy atomizers divided to four classes, liquid and gas energy, mechanical, vibrational, and electrical energy [1]. Our focus is mostly on atomizers in gas energy (pneumatic acceleration), including vibrational (ultrasonic) and electrical energy (electrostatic) devices. Thus, spray pyrolysis is usually classified as air blast or pressurized spray pyrolysis [2], ultrasonic spray pyrolysis [3] and electrostatic spray pyrolysis [4].

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In electrostatic spray pyrolysis, different spraying modes are acquired which were classified by Cloupeau and Prunet-Foch [5] as dripping, micro-dripping, spindles, con-jets and simple jets. Each mode has various droplet size distributions that have effects on film properties.

There are some reports on modifying the process of SP to overcome limitations which are encountered with corona spray pyrolysis [6], improved spray pyro-hydrolysis [7] and micro-processor based spray pyrolysis [8]. This is accomplished by using different atomizers, resulting in different droplet velocities and sizes which impact the properties of the deposited film [9].

2.2. Transportation and evaporation of solvent

The transportation of aerosol droplets from the atomizer to the substrate is part of the deposition process during which shrinkage of droplets occurs as a result of solvent evaporation. The perfect situation is for droplets of precursor reaching the target just as its evaporation has been completed [10]. Filipovic [11] identified four forces which affect aerosol formation, including gravitational, electrical, stroke, and thermophoretic forces. Each of these forces varies substantially as the droplet undergoes continuous vaporization during its path toward the substrate.

Computer modeling of the spraying process should include variation in these forces. Chen [12] calculated the flight time of droplets in an ESD process for small distances which allowed for assumptions such as constant electric fields, but ignored assigning a solvent evaporation parameter. Based on interfacial tension between substrates, gases and droplet liquids, spreading of droplets varied. The rate of droplet flattening was reduced as the viscosity of the solution was elevated [12]. Lampkin [13] has studied the aerodynamics of nozzles in which the velocity and direction of atomization are important factors in droplet impact on targets.

Some simulations have been reported on the effect of impact properties (droplet velocity and size) on the fattening ratio in the scale of atoms. Shimizu et al. [14] has evaluated the fattening ratio for Al droplets and drawn the conclusion that the flattening ratio is enhanced by increasing droplet size and velocity.

The evaporation of solvent occurs parallel to droplet transportation, landing, and spreading on the substrate. This effect leads to droplet size reduction and then formation of precipitates. In the electrostatic spray deposition (ESD) process, droplet disruption may be observed during evaporation defined as the splitting of one charged droplet to a few smaller ones when its charge density reaches the maximum amount [12]. Depending on temperature and droplet size, various types of products reach the target surface (wet droplet, dry precipitate, vapor, or powder) [10,15] which will be discussed later.

The flow rate of precursor to the nozzle controls the spray rate and amount of deposited film on the target. The flow rate (f) of the aerosol itself is affected by a proportionality constant K and the square root of liquid characteristics such as viscosity (μ), vapor pressure (P), and surface tension (σ) [16]. The following equation shows this correlation:

$$f = K \sqrt{\frac{P}{\mu\sigma}} \quad (1)$$

Based on the above equation, if any enhancement of the viscosity occurs in the solvent, the flow rate changes accordingly. As any additives in the precursor causes changes in the viscosity and surface tension of solvent, the flow rate varies through the nozzle and must be accounted for when designing spray deposition experiments [16].

Perednis et al. have studied the flow rate parameter in ESD and pressurized spray deposition (PSD) [17]. Their investigation shows that changing the flow rate of precursor has a significant influence on the process. As a result, ESD (with the normal flow rate of 1–8 mL/h) is more sensitive to flow rate parameters than PSD (normal range of flow rate 30–120 mL/h). At lower feed rate of precursor in the ESD process, denser homogeneous thin films can be regularly synthesized. In both processes though, the higher the flow rate, the higher the possibility of film cracking, due to many of the previously noted processes. The related concept of droplet formation and droplet entrainment is illustrated in Fig. 1 showing the formation of deposits from TiO₂ aerosol-derived films [18]. The effects of droplet size, evaporation rate, substrate distance, and flow rates can be illustrated as having major consequences for deposited films.

2.2.1. Particles

The previously discussed pyrolysis techniques describe liquid precursors carrying metallic or polymeric solutes being sprayed. However, the original spray deposition techniques were originally conceived for nano-scale powders in suspension [19]. Preparation of field effect transistors [20], carbon nanotubes [21], and thin films [22] have been carried out by the aerosol method. To produce particles and powders, a typical spray pyrolysis setup as discussed before (and similar to thin film synthesis set ups) includes precursor solutions, aerosol generators or atomizers, reactors or hot furnaces and collectors for product [23].

Aerosols are defined as a suspension of solid or liquid particles in a gas medium. To prepare particles by aerosols, two different methods are applicable which include vapor deposition techniques and spraying of a liquid-phase precursor. Preparing particles by generating aerosols has several advantages: controllable crystallite size, morphology and composition of particles, low cost operation, continuous operation, and high rate production [24]. Recent improvements in the designs of spraying nozzles prevent issues such as clogging and breaking of the nozzle by pressure buildup. Once an aerosol is formed, the spray is directed toward a furnace in which solvent evaporation, component diffusion, forming precipitates, and pyrolysis may occur. A substrate for film formation may be housed in such furnaces.

Size, size distribution and morphology of particles are manipulated by controlling the droplets in the aerosol, and their environment of atomization. Atomization is classified as jet, swirl, jet-swirl, pneumatic, rotary, acoustic, ultrasonic and electrostatic [1] depending on the nozzle geometry and spray technique. There are some review papers on synthesizing particles via spray pyrolysis techniques [19,24,25]. Of note is the review by Jung et al. [25d], which points to enhancement of research work on spray pyrolysis in recent years.

2.3. Spray pyrolysis techniques – flame spray pyrolysis

A search for “flame spray synthesis” on ScienceDirect returns 1899 articles as of September 26th, 2013 since 2010; More than 450 articles came out each year, and has covered topics including fuel cells, thin films, photocatalytic activities, NO_x emissions, diesel fuel, calcium phosphate, heat transfer, ZnO nanoparticles, and carbon nanotubes. Flame spray pyrolysis (FSP) utilizes similar methodology at the previously listed spray techniques; precursors can be liquid/liquid phase, or a suspension of particles in a liquid which is sprayed via an atomizer. In flame-spray pyrolysis, the outlet stream is passed through a methane or hydrogen-fueled flame, resulting in fast combustion, solvent evaporation and pyrolysis, affording nanoparticles of varying morphologies. Temperatures of spraying can reach 2000 K at the outlet; and the resulting spray can be trapped in a collector or subjected to further pyrolysis.

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