Chapter 2
Combustion Synthesis

The Science of Nanomaterials is proving to be one of the most attractive and promising fields for technological development in this century. In the scientific literature several terms related to Nanoscience can be found, of which it is worth highlighting nanoparticles, nanocrystals, nanofibers, nanotubes and nanocomposites. In fact, all these are related to nanostructured materials, which have well-defined structural features. The physical and chemical properties of materials at the nanometer scale (usually set in the range of 1–100 nm) are of immense interest and increasing importance for future technological applications. Nanostructured materials often exhibit different properties when compared to other materials.

The relationship between particle size and properties has been known since the nineteenth century, when Faraday showed that the color of colloidal Au particles can be modified depending on their size. However, despite the long history of their discovery, the interest in nanoparticles has only increased significantly in the last 15 years. The research activities related to this area were driven by the ability to control material properties by controlling the size of the particles.

The nanotechnology wave will likely change the way materials and devices are produced in the future. The ability to synthesize crystallites at the nanometer scale with precisely controlled size and composition and to assemble them into large structures with unusual properties and functions, will revolutionize all segments of material manufacturing for industrial applications. Among the main techniques for generating nanoparticles via the wet chemical route, combustion synthesis is the one that stands out.

Solution combustion synthesis (SCS) is an effective method for the synthesis of nanoscale materials and has been used in the production of various ceramic powders for a variety of advanced applications.

Ceramic oxide powders at the nanoscale using SCS can be prepared by the combination of metal nitrates in an aqueous solution with a fuel. Glycine and urea, in particular, are suitable fuels because they are amino acids that can act as a complexing agent of the metal ion in the solution and also serve as fuel for the synthesis of nanocrystalline metal oxides. This method can directly produce the
desired final product, although in some cases, a subsequent heat treatment of the synthesized powder is needed to promote the formation of the required phase.

The properties of the resulting powders (crystalline structure, amorphous structure, crystallite size, purity, specific surface area and particle agglomeration) depend heavily on the adopted processing parameters. It is surprising, however, how little information is available on the parameters of combustion and reaction mechanisms, despite all SCS studies emphasizing the characterization of the synthesized materials.

In the case of the synthesis of alumina, chrome, nickel, iron and nanocrystalline cobalt oxides using the solution combustion technique, for example, we lack, so far, a deep understanding of the influence of the fuel-oxidant ratios well as a model of the thermodynamic variables associated with enthalpy, adiabatic flame temperature and the total number of moles of gas generated related to the powder characteristics, such as crystallite size and surface area.

### 2.1 Nanopowder Synthesis

There are numerous ways in which ceramic powders can be synthesized: solution, solid-solid or solid-gas processes. The solution processes have been increasingly used due to their peculiar characteristics. The goal of all these processes is the production of high purity powders with fine particle sizes, usually a small aggregation and/or agglomeration and produced at low costs. The process of choice, however, depends on the material in question, the application and the required amount of reagents and products.

A method for the preparation of highly pure and homogeneous powders, especially interesting for obtaining nanocrystalline powders such as ceramic oxides, is solution combustion synthesis (SCS).

Solution combustion synthesis makes use of salts, such as nitrates, metal sulfates and carbonates, as oxidants and, reducing reagents, fuels such as glycine, sucrose, urea, or other water soluble carbohydrates. Nitrate acts as an oxidizer for the fuel during the combustion reaction. The powder can be a pyrolysed product of a single phase, but usually it is a combination of metal oxides and in some cases it needs subsequent heat treatment to form single-phase products, which are usually the results required in this process.

Solution combustion synthesis is a method based on the principle that once a reaction is initiated under heating, an exothermic reaction occurs that becomes self-sustaining within a certain time interval, resulting in a powder as final product. The exothermic reaction begins at the ignition temperature and generates a certain amount of heat that is manifested in the maximum temperature or temperature of combustion. Solution combustion synthesis has the advantage of rapidly producing fine and homogeneous powders. Since it is an exothermic, auto-propagated process, and with a high heat release rate, it can be explosive and should be undertaken with extra precautions.
Solution combustion synthesis is a quick and easy process, with as main advantages the saving of time and energy. This process is used directly in the production of high purity, homogeneous ceramic oxide powders. This method is versatile for the synthesis of a wide size range of particles, including nanometer size alumina powders, as reported by Patil and Mimani [1]. Interestingly, the combustion of a mixture of redox metal nitrate-glycine-nitrate ammonium acetate or mixtures of metal-aluminum nitrate-urea combustion systems, showed no presence of a flame for obtaining oxide nanoparticles. The foundation for the combustion synthesis technique lies in the thermodynamic concepts used in the field of propellants and explosives, and its extrapolation to the combustion synthesis of ceramic oxides and its thermodynamic interpretation are discussed extensively by several researchers. The success of this process is closely linked to the mix of constituents of a suitable fuel or complexing agent (e.g., citric acid, urea, and glycine) in water and an exothermic redox reaction between the fuel and the oxidant (e.g., nitrates).

Table 2.1 Some oxides prepared by combustion in solution

<table>
<thead>
<tr>
<th>Material</th>
<th>Fuelab</th>
<th>Particle size</th>
<th>Application</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>U</td>
<td>4 μm</td>
<td>Abrasive</td>
<td>[3]</td>
</tr>
<tr>
<td>MA₆O₄</td>
<td>AM + U/CH/ODH/GLI</td>
<td>15–28 nm</td>
<td>Catalyst support</td>
<td>[4]</td>
</tr>
<tr>
<td>M/MgAl₂O₄, M = Fe-Co/Ni</td>
<td>U</td>
<td>10 nm</td>
<td>Catalyst</td>
<td>[5]</td>
</tr>
<tr>
<td>Co²⁺/Al₂O₃</td>
<td>U</td>
<td>0.2–0.3 μm</td>
<td>Pigment</td>
<td>[6]</td>
</tr>
<tr>
<td>Eu⁴⁺/Y₃Al₅O₁₂</td>
<td>U</td>
<td>60–90 nm</td>
<td>Red phosphorus</td>
<td>[7]</td>
</tr>
<tr>
<td>Ce₁₋ₓTbₓMgAl₁₁O₁₉</td>
<td>CH</td>
<td>10–20 μm</td>
<td>Green phosphorus</td>
<td>[8]</td>
</tr>
<tr>
<td>M/Al₂O₃, M = Pt, Pd, Ag</td>
<td>U</td>
<td>7–10 nm</td>
<td>Catalyst</td>
<td>[9, 10]</td>
</tr>
<tr>
<td>Pd/Al₂O₃</td>
<td>U</td>
<td>10–18 nm</td>
<td>Catalyst</td>
<td>[11]</td>
</tr>
<tr>
<td>CeO₂/ZrO₂</td>
<td>ODH</td>
<td>18 nm</td>
<td>Oxigen storage</td>
<td>[12]</td>
</tr>
<tr>
<td>M/CeO₂, M = Pt, Pd, Ag</td>
<td>ODH</td>
<td>1–2 nm</td>
<td>Catalyst</td>
<td>[13, 14]</td>
</tr>
<tr>
<td>Ce₁₋ₓPtₓO₂</td>
<td>CH</td>
<td>4–6 nm</td>
<td>H₂-O₂ combination catalyst</td>
<td>[15]</td>
</tr>
<tr>
<td>Ni-YSZ, (Ni,Co/Fe/Cu) -YSZ</td>
<td>U</td>
<td>~40 nm</td>
<td>Combustion cell anode (SOFC)</td>
<td>[16]</td>
</tr>
<tr>
<td>LaSrFeO₃</td>
<td>CH/ODH</td>
<td>20–30 nm</td>
<td>SOFC cathode</td>
<td>[17]</td>
</tr>
<tr>
<td>LaCrO₃</td>
<td>U</td>
<td>20 nm</td>
<td>Interconnection for SOFC</td>
<td>[18]</td>
</tr>
<tr>
<td>LiCo₀.₃M₀.₇O₂</td>
<td>U</td>
<td>5–10 μm</td>
<td>Lithium battery</td>
<td>[19]</td>
</tr>
<tr>
<td>MF₂O₄/BaFe₁₂O₁₉</td>
<td>ODH</td>
<td>60–100 nm</td>
<td>Magnetic oxide</td>
<td>[20]</td>
</tr>
<tr>
<td>BaTiO₃</td>
<td>GLI/AC</td>
<td>18–25 nm</td>
<td>Dielectric material</td>
<td>[21]</td>
</tr>
<tr>
<td>Pb(Zr,Ti)O₃</td>
<td>AC</td>
<td>60 nm</td>
<td>Piezoelectric material</td>
<td>[22]</td>
</tr>
<tr>
<td>ZnO</td>
<td>U</td>
<td>&lt;100 nm</td>
<td>Varistor</td>
<td>[23]</td>
</tr>
</tbody>
</table>

ab U urea, CH carbohydrazides, ODH oxalildihidrazida, GLI glycine, AC citric acid, AM metal acetate
In fact, the reaction mechanism of the combustion is very complex. There are several parameters influencing the reaction such as the type of fuel, fuel-oxidizer ratio, use of excess oxidizer, ignition temperature, and amount of water contained in the precursor mixture. In general, a good combustion synthesis does not react violently, produces non-toxic gases and acts as a complexant for metal cations.

The characteristics of the powders, such as crystallite size, surface area, nature of agglomeration (strong and weak), is governed mainly by the enthalpy and flame temperature generated during combustion, which in turn is dependent on the nature of the fuel and the kind of fuel-oxidizer used in the reaction.

The rapid generation of a large volume of gases during combustion dissipates the heat from the process and limits the temperature rise, reducing the possibility of premature sintering between the primary particles. The generation of gases also helps limit interparticle contact, resulting in a more powdery product.

The combustion technique appears to be controlled by the mass of the mixture and the volume of the container. Studies conducted by Kingsley and Patil [2] demonstrated that the mass/volume ratio is critical for the occurrence of combustion synthesis, as compositions with less than 5 g in containers of 300 mL did not undergo the ignition process.

The solution combustion synthesis method has proven to be a great technique to obtain various types of oxides at the nanometer scale and is used for a variety of technological applications, as can be seen in Table 2.1. This wide range of oxides is prepared with an eye on their magnetic, mechanical, dielectric, catalytic, optical and luminescent properties.

### 2.2 Combustion Parameters

The main parameters of combustion that have been widely investigated in the literature are: type of flame, temperature, generated gases, air-fuel-oxidant ratio and chemical composition of the precursor reagents.

#### 2.2.1 Flame Types

The formation of the combustion flame arises through the release of heat from the chemical burning of the transformed substances. Combustion generates characteristic types of flames as shown below in Table 2.2.

SCS synthesis, in general, under controlled conditions, generates a peculiar kind of burning or smoldering type flame, depending on the employed fuel and oxidizer-fuel ratio. The burning flame can endure for seconds or even minutes, while the smoldering flame does not rise or is extinguished in a few seconds. The type of flame in the combustion plays an important role in controlling the particle size of as-synthesized powders.
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For example, Fig. 2.1 represents a SCS process using Ca(NO_3)_2, Al(NO_3)_3 and β-alanine and a smoldering flame is observed. In Fig. 2.2, the same materials were used but urea was used as an additional fuel, and flaming occur.

It should be noted that in any combustion process the mixture of the reactants (fuel and oxidizer) may be hypergolic (ignition by contact) or the ignition may be controlled by an external source. These conditions are crucial for generating the flame.

There is a dependence on the type of flames, linked to the fuel used, as can be seen in the use of urea, which acts more reactive leading to the formation of flame glow, than a solution in the presence of glycine, characterized by smoldering. The reactivity of the combustion reaction is dependent on the ligand groups of the molecules of the fuel and the compositional ratio of fuel and oxidant.

### 2.2.2 Characteristic Temperatures

During the combustion synthesis reaction, there are four important temperatures that can affect the reaction process and final product properties:

* **Initial temperature** ($T_0$) is the average temperature of the reagent solution before the reaction is ignited;

* **Ignition temperature** ($T_{ig}$) represents the point at which the combustion reaction is dynamically activated without an additional supply of external heat;

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**Table 2.2 Flame types [3]**

<table>
<thead>
<tr>
<th>Type</th>
<th>Temperature</th>
<th>Burning rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flaming (gas phase)</td>
<td>Over 1,000 °C</td>
<td>–</td>
</tr>
<tr>
<td>Smouldering (Solid-gas phase)</td>
<td>Below 1,000 °C</td>
<td>~cm/s</td>
</tr>
<tr>
<td>Explosive type</td>
<td>High temperature and pressure</td>
<td>4000–8000 m/s</td>
</tr>
</tbody>
</table>

**Fig. 2.1** Smoldering flame type: the evolution of combustion reaction containing Ca(NO_3)_2, Al(NO_3)_3 and β-alanine [24]
Adiabatic flame temperature \((T_{ad})\) is the maximum combustion temperature achieved under adiabatic conditions;

Maximum flame temperature \((T_m)\) is the maximum temperature reached in the actual configuration, i.e., under conditions that are not adiabatic.

The calculation of the ignition temperature is not as simple as the adiabatic flame temperature. The ignition temperature is a complex quantity, not only strictly related to the thermodynamics and thermal physics of the system, but also the details of the reaction mechanism. As a general rule, the ignition process is obtained with a small, but significant amount of reagent solution. When this solution is rapidly heated above the temperature where the chemical reaction rate is high enough, you get a heat release rate greater than the dissipation of heat.

The flame temperatures are influenced by a large number of factors. The flame temperature can be increased with the addition of excess oxidant, such as nitrate ammonium, or the increase of the fuel-oxidant. The adiabatic flame temperature can be calculated using the heat capacity of the products, the ignition temperature and the heat of combustion, assuming that no heat is lost in the system. The flame temperature measurements are almost always much smaller than the calculated adiabatic values. Irradiated losses, incomplete combustion and air heating contribute to a decrease in the actual flame temperature.

### 2.2.3 Gas Generation

It is a well-established fact that in combustion synthesis, the powder morphology, particle size and surface area are directly related to the amount of gases that escape during combustion. The gases break large clusters and create pores...
between particles. In fact, the clusters are disintegrated in conditions of high pro-
duction of combustion gases and in these conditions more heat is released from the
system, hindering particle growth.

The difference in particle size, using different fuels, depends on the number of
moles of gaseous products released during combustion. Thermodynamic modeling
shows an increase in gas generation with an increase of the fuel-oxidant.

### 2.2.4 Atmosphere

The effect of atmosphere composition and properties of combustion products
synthesized in solution is still poorly understood and studied in the literature.
The interference of the environment (O₂ and CO₂ in the air) and insufficient
reaction temperatures result in an incomplete combustion, forming products
with various metastable solid phases instead of the pure oxide and NOₓ or
CO gas.

Experiments carried out in argon atmosphere allowed the synthesis of single
phase magnetite (Fe₃O₄). Magnetite reacts with atmospheric O₂, resulting in the
formation of the Fe₂O₃ phase.

### 2.2.5 Fuel-Oxidant Ratio

A fuel is a substance capable of burning the CH bonds (electrons acceptor). An
oxidant is a substance that helps in burning, providing oxygen (electrons donor).
Only when the oxidizer and fuel are intimately mixed in an appropriate proportion
can an exothermic chemical reaction be initiated that generates substantial heat.
The temperature reached when the reaction starts in the oxidizer and fuel solution,
is called the ignition temperature.

The ratio of fuel and oxidizer is considered one of the most important parame-
ters in determining the properties of synthesized powders obtained by combustion.
Product properties such as crystallite size, surface area, morphology, phase, degree
and nature of agglomeration, are generally controlled by adjusting the fuel-oxidant
ratio.

The fuel-oxidant ratio determines the influence of gases on the morphology of
the particles. The pore size depends on the fuel-oxidant ratio, because the greater
the amount of fuel, the larger the pore size of the particles.

Recent research on SCS has investigated the role of fuel in the control of par-
ticle size and microstructure of the products under different fuel-oxidant ratios
(Table 2.3). The fuel-oxidant ratio, however, is not always calculated using a ther-
modynamic modeling and/or theory of the propellants.
2.2.6 Chemical Composition of Precursor Chemicals

The type and amount of chemicals used in the reactions exert effect on the characteristics of the resulting powders. The solubility of the fuel, the presence of water and type of fuel used, are critical. In solution, mixtures of metal nitrates (oxidizers) and urea or glycine (fuel) are broken down quickly via deflagration burning or combustion.

Excellent product homogeneity is achieved by the use of chemical precursors intimately mixed. That happens, in general, when oxidants and fuels are dissolved in water. The fuel also serves as complexing agent limiting the precipitation of individual precursor components prior to ignition.

The addition of an inert salt in a mixture of redox solution for combustion synthesis may result in the formation of well dispersed nanoparticles with

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**Table 2.3** Study of the influence of fuel-oxidant ratio in obtaining ceramic oxides by SCS

<table>
<thead>
<tr>
<th>Material</th>
<th>Fuela</th>
<th>Particle size</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al2O3</td>
<td>U</td>
<td>72–141 nm</td>
<td>[25]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>33–56 nm</td>
<td>[26]</td>
</tr>
<tr>
<td>Al2O3</td>
<td>GLI</td>
<td>84–123 nm</td>
<td>[27]</td>
</tr>
<tr>
<td>Al2TiO5</td>
<td>U</td>
<td>~927 nm</td>
<td>[28]</td>
</tr>
<tr>
<td>Ce1−xZrxO2</td>
<td>CH/ODH</td>
<td>5–18 nm</td>
<td>[12]</td>
</tr>
<tr>
<td>CeO2</td>
<td>GLI</td>
<td>3–28 nm</td>
<td>[29]</td>
</tr>
<tr>
<td>CoAl2O4</td>
<td>AC</td>
<td>10–110 nm</td>
<td>[30]</td>
</tr>
<tr>
<td>CoO/Co3O4/Co</td>
<td>GLI</td>
<td>23–90 nm</td>
<td>[31]</td>
</tr>
<tr>
<td>Cr2O3/Co3O4</td>
<td>U/GLI</td>
<td>18–50 nm</td>
<td>[32]</td>
</tr>
<tr>
<td>CuO-CeO2</td>
<td>U</td>
<td>5–24 nm</td>
<td>[33]</td>
</tr>
<tr>
<td>Fe2O3-γ</td>
<td>GOL</td>
<td>169–228 nm</td>
<td>[34]</td>
</tr>
<tr>
<td>Fe3O4/Fe2O3-α</td>
<td>U</td>
<td>20–105 nm</td>
<td>[35]</td>
</tr>
<tr>
<td>La0.84Sr0.16CrO3</td>
<td>GLI</td>
<td>5–40 nm</td>
<td>[36]</td>
</tr>
<tr>
<td>Li2TiO3/LiNO3/TiO2</td>
<td>U/GLI/AC</td>
<td>~30 nm</td>
<td>[37]</td>
</tr>
<tr>
<td>LnCrO3</td>
<td>GLI</td>
<td>11–59 nm</td>
<td>[38]</td>
</tr>
<tr>
<td>MgAl2O4</td>
<td>U/S</td>
<td>3–32 μm</td>
<td>[39]</td>
</tr>
<tr>
<td>NiO/NiFe2O4/Cu</td>
<td>GLI</td>
<td>&lt;10 nm</td>
<td>[40]</td>
</tr>
<tr>
<td>NiO/Ni</td>
<td>GLI</td>
<td>4–18 nm</td>
<td>[41]</td>
</tr>
<tr>
<td>Ni-YSZ (Cermet)</td>
<td>CH</td>
<td>250–800 nm</td>
<td>[16]</td>
</tr>
<tr>
<td>Ni-YSZ</td>
<td>U</td>
<td>36–545 nm</td>
<td>[42]</td>
</tr>
<tr>
<td>Pb(Zr0.6Ti0.4)O3</td>
<td>PVA</td>
<td>100–400 nm</td>
<td>[43]</td>
</tr>
<tr>
<td>SrB12Nb2O9</td>
<td>U</td>
<td>22–145 nm</td>
<td>[44]</td>
</tr>
<tr>
<td>ThO2</td>
<td>GLI</td>
<td>15–23 nm</td>
<td>[45]</td>
</tr>
<tr>
<td>Y2O3</td>
<td>GOL</td>
<td>3–17 nm</td>
<td>[46]</td>
</tr>
<tr>
<td>Y2SiO5/Y3Al5O12/Y2O3/BaMgAl10O27</td>
<td>U/GLI/CH</td>
<td>&gt;200 nm</td>
<td>[47]</td>
</tr>
<tr>
<td>YFeO3</td>
<td>GLI</td>
<td>6–50 nm</td>
<td>[48]</td>
</tr>
<tr>
<td>ZnO</td>
<td>U</td>
<td>&lt;100 nm</td>
<td>[23]</td>
</tr>
<tr>
<td>ZrO2</td>
<td>PVA</td>
<td>10–160 nm</td>
<td>[49]</td>
</tr>
</tbody>
</table>

*a U urea, GLI glycine, CH carboxyldrazides; ODH oxalildihdrazida, AC citric acid, GOL glycol, S sucrose, PVA polyvinyl acid
a more prominent increase in surface area. The addition of salt should break the three-dimensional porous structure, typical of the resulting powders through combustion and act as an inhibitor of the agglomeration. The inorganic salt is generally low cost when compared with organic salts, readily soluble in water, thermally stable at high temperatures, easily removed from the product-mix as-prepared and recyclable.

2.3 Fuels

Glycine (NH$_2$CH$_2$COOH) is one of the cheapest amino acids and is known to act as a complexing agent for a large amount of metallic ions. The glycine molecule has a carboxylic acid group located at one end of the chain and an amino group at the other. Both groups can participate in the complexation of metal ions. Alkaline and earth alkaline cations are most effectively complexed by the carboxylic acid groups, while many transition metals are complexed more effectively through the amino group. The high solubility of metal ions in question, as well as the high relative viscosity of the precursor solution, tends to inhibit the precipitation of heterogeneous compounds.

The amino acids become bipolar (zwitterionic or amphoteric) when in aqueous solution by presenting positive and negative charges. This bipolar character of the glycine molecule in solution can effectively act as a complexing agent for metal ions of various sizes, which helps to prevent selective precipitation and maintain compositional homogeneity among the constituents. In combustion synthesis glycine serves as fuel during the reaction, being oxidized by nitrate ions.

Urea (NH$_2$CONH$_2$) is an attractive fuel for originating the formation of powders with crystallite sizes in the submicron/nanosized range and act as a complexing agent for metal ions because it contains two amino groups located at the extremes of its chemical structure. Deshpande et al. found that the chemical activity of the ligand-NH$_2$ promotes more vigorous combustion reactions among various fuels studied with iron nitrate.

2.4 Oxidants

Nitrates are chosen as metal precursors, not only because they are fundamental to the combustion method, for providing the metal ion, but also because of their great water solubility, allowing a greater homogenization.

Most oxides synthesized by combustion can be obtained by combining a metal nitrate and fuel. Groups (NO$_3$)—act as oxidizing agents.

Ammonium nitrate (NH$_4$NO$_3$) is used in combustion reactions to act as extra-oxidant and without changing the proportion of other participants of the chemical reaction. Another interesting feature is its low cost.
The excess addition of ammonium nitrate produces an increase in combustion gas, and the effect of expanding the microstructure and eventually increasing the surface area of the produced powder. As can be seen, the decomposition of ammonium nitrate generates, in part, the same gases obtained for the pair of aluminum nitrate and glycine, according to Eq. 2.1.

$$2NH_4NO_3 (s) \rightarrow 2N_2 (g) + 4H_2O (g) + O_2 (g) \quad (2.1)$$

The ammonium dichromate—(NH₄)₂Cr₂O₇—is known to decompose and generate exothermic autocatalytic Cr₂O₃, N₂, and H₂O. This salt has advantages over the nitrate because it decomposes into chromium at a lower temperature (170 °C) and is more exothermic (ΔH: ±0.4–476.4 kJ/mol).

References

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