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SYNTHESIS OF NANO-MATERIALS FOR VARIETY OF APPLICATIONS USING SOLUTION COMBUSTION SYNTHESIS (SCS)

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ABSTRACT :

Nano-science and technology has emerged as a frontier area of research today and hence a demand to prepare the nano-materials for the variety of application has been increased significantly to a laboratory as well as industrial level. Therefore, to fill-up these demands a synthesis technique is developed by Prof. K.C. Patil of Indian Institute of Science, Bangalore, which allows production of nano-materials on a wide scale. The technique named solution combustion synthesis (SCS) although having all the advantage of Self-propagating High temperature Synthesis (SHS); it is rather simple, economical and fast technique. The article presents brief details of technique to get started with SCS.

KEYWORDS: Nanotechnology, Nano-materials, Solution combustion

IMPORTANCE OF NANOMATERIALS:

Nano-science and technology has emerged as a frontier area of research today. Research in “Nano-chemistry”, chemistry of nano-materials, has resulted in the developments of newer methods of synthesis of materials with desired structure, composition, and properties of nano-materials and their related applications. Currently considerable interest in nanocrystalline oxide materials exists due to their unusual properties. It has been found that smaller the particles,

- higher the catalytic activity (Pt/Al_2O_3)
- higher the photocatalytic activity (TiO_2)
- higher the electrical conductivity of ceramics (CeO_2)
- lower the electrical conductivity of metals (Cu, Ni, Fe, Co, and Cu alloys)

All of these improvements or unusual transitions of properties in nano-materials are due to its decreased particle size which results in some remarkable phenomenon. For example, the large surface area to volume ratio of nano-materials leads to their use as highly active catalysts.

Optical and electrical properties in these materials show abnormal behavior due to a phenomenon known as quantum confinement. Due to fine nature of nano-materials, there exists a high surface area and high surface energy leading to its excellent sintering characteristics. These fine powders, due to their excellent sintering characteristics, are useful in ceramics and composites to achieve the desirable microstructure at comparatively lower temperatures. In addition, easier dispersion of these ultrafine particles in various fluids allows the fabrication of corrosion resistant coatings and thin films.

PREPARATIVE METHODS :

The synthesis of materials with desired composition, structure, and properties for specific applications is one of the major challenges faced by materials scientists. Although one can improve a well-organized approach to the synthesis of oxide materials, accidents has played an important role in making new materials. Besides, a practical synthesis of materials requires knowledge of crystal chemistry, besides thermodynamics, phase equilibrium, and reaction kinetics. For example, the physicochemical properties of many materials are determined by the choice of synthetic methods and therefore could not be anticipated on accidently evolved methods. Selection of the synthetic route is crucial to control the composition, structure, and morphology of a chosen material.

Oxide materials are usually prepared by solid-state reactions, i.e., either by the ceramic method or by precipitation from solution and subsequent decomposition. A variety of metal oxides, both simple and complex, is prepared by the conventional ceramic method. This involves the mixing of constituent metal oxides, carbonates, etc., and their repeated heating and grinding. These methods are used on both laboratory and industrial scale. However, there is an increasing demand for alternate routes to the synthesis of oxide materials that give superior properties when compared with those available from conventional methods. The need for alternate synthesis routes for oxide materials has arisen because of inherent problems relating to:

- Inhomogeneity of the products obtained by ceramic methods
- Incorporation of chemical impurities during repeated grinding and heating operations.
- Impurities have a harmful effect on high - temperature mechanical behavior of engineering ceramics and on the electrical properties of electro-ceramics.
- Coarseness of particles obtained from conventional routes, makes them unsuitable for coatings.

Reproducibility in fabrication of a component becomes difficult due to non-uniform powder compositions since it certainly causes chemical inhomogeneity and voids in microstructure of final product. Greater purity and homogeneity from novel methods can lead to improved physical properties. The present trend in material synthesis is to avoid physical methods in order to have a better control of stoichiometry, structure, and phase purity of metal oxides. Soft chemical routes are now increasingly becoming popular to prepare a variety of oxides including nanocrystalline oxide materials. These approaches make use of simple chemical reactions like co-precipitation, sol–gel, ion exchange, hydrolysis, acid leaching, and so on, at considerably low temperatures compared to the ceramic method. Use of precursors, intercalation reactions, electrochemical methods, hydrothermal process, and self-propagating high temperature synthesis (SHS) are some of the other existing methods. Among these methods, combustion or fire synthesis (i.e. SHS) is quite simple, fast, and economical.

COMBUSTION SYNTHESIS :

Combustion synthesis or fire synthesis is also known as self-propagating high-temperature synthesis (SHS). All self-propagating high-temperature synthesis reactions are redox reactions; however, not all redox reactions need be SHS reactions. For the reaction to be self-propagating, the heat evolved should be more than the heat required for initiating the combustion. A redox reaction involves simultaneous oxidation and reduction processes. The classical definition of oxidation is addition of oxygen or any other electronegative element (nonmetal), while reduction is addition of hydrogen or any other electropositive element (metal). In other words, one could also define redox as “OIL-RIG” i.e. Oxidation Is Loss (of electrons) and Reduction Is Gain (of electrons). The term combustion covers flaming (gas-phase), smouldering (solid-gas) as well as explosive reactions. It can be linear combustion or volume combustion. In linear combustion, the burning surface recedes from top to bottom in layers, whereas in volume combustion, the entire reaction mixture ignites to burn with a flame.

Although SHS, has been successfully used to make non-oxide materials (carbides, nitrides, borides, silicides), its application for synthesis of technologically useful oxide materials (refractories, magnetic, semiconductors, dielectric, catalysts, sensors, phosphors) was delayed due to economic reasons. Furthermore, it being a solid-state method, phase purity and particle size control is not possible and due to its high-temperature course, it is not suitable for the preparation of nanocrystalline materials. In this context, a low-temperature initiated combustion method [1, 2] developed by Patil et al. at Indian Institute of Science, Bangalore was a breakthrough. This low-temperature initiated self-propagating combustion process is different from the well-known Pechini (citrate process) which uses external heating at high temperatures to burn away the extra carbon [3]. Combustion process is different from pyrolysis since once ignited it does not require external heating.

In the synthesis of nano-materials by soft routes, there are two approaches: (i) breaking-down and (ii) building-up processes. Solution combustion synthesis (SCS) of nanocrystalline oxide materials while appearing to be a breaking-down (exothermic) process is in fact an integrated approach, as the desired oxide products nucleate and grow from the combustion residue. Prof. Patil unexpectedly discovered SCS of oxide materials during the reaction between aluminum nitrate and urea. A mixture of $Al(NO_3)_3$-$9H_2O$ and urea solution, when rapidly heated around 500°C in a muffle furnace, foamed and ignited to burn with an incandescent flame yielding voluminous white product which was identified as α-Al_2O_3 [4].

FUNDAMENTALS OF SOLUTION COMBUSTION SYNTHESIS (SCS) :

Combustion being an exothermic redox chemical reaction requires an oxidizer and a fuel. The oxidizers used are water-soluble metal nitrates; the fuels employed are readily available compounds like urea, glycine, metal acetates, and hydrazides, all of which are also water-soluble. Synthesis of metal oxides is achieved by rapidly heating an aqueous solution containing stoichiometric quantities of the redox mixture. Calculation of stoichiometry is very critical and important to solution combustion synthesis. This calculation is based on the principles used in propellant chemistry and consists of balancing elemental oxidizing and reducing valences of the compounds utilized in combustion. To understand the highly exothermic nature of combustion reaction, concepts used in propellant chemistry were employed [5]. A solid propellant contains an oxidizer and a fuel. The specific impulse (I_{sp}) of a propellant, which is a measure of energy released during combustion is given by the ratio of thrust produced per pound of the propellant. It is expressed as

$$I_{SP} = k\sqrt{\frac{T_c}{\text{Molecular wt. of gaseous product}}}$$

The highest heat T_c (chamber temperature in the rocket motor) is produced when the equivalence ratio (φ_e = oxidizer/fuel ratio) is unity.

$$\Phi_e = \frac{\text{Total oxidizing valency of reactants}}{-\text{Total reducing valency of reactants}}$$

A mixture is said to be stoichiometric when $\varphi_e = 1$, fuel lean when $\varphi_e > 1$, and fuel rich when $\varphi_e < 1$. Stoichiometric mixtures produce maximum energy.

The oxidizer/fuel molar ratio (O/F) required for a stoichiometric mixture ($\varphi_e = 1$) is determined by summing the total oxidizing and reducing valencies in the oxidizer compounds and dividing it by the sum of the total oxidizing and reducing valencies in the fuel compounds. In this type of calculation oxygen is the only oxidizing element; carbon, hydrogen, and metal cations are reducing elements and nitrogen is neutral. Oxidizing elements have positive valencies and reducing elements have negative valencies.

Now, for example, consider the SCS of cerium nitrate with glycine as fuel. Accordingly, the elemental valency of C, Ce, and H is +4, +3, and +1, respectively, and oxidizing valency of oxygen is taken as -2. The valency of nitrogen is considered to be zero. Based on this concept, the oxidizing valency of cerium nitrate and the reducing valency of glycine are

Oxidizing valancy of $Ce(NO_3)_3.6H_2O$,

$= 1_{Ce} \times (3) + 3_N \times (0) + 15_O \times (-2) + 12_H \times (1)\} = 3 + 0 - 30 + 12 = -15.$

Reducing valancy of $C_2H_5NO_2$,

$= 2_C \times (4) + 5_H \times (1) + 1_N \times (0) + 2_O \times (-2) = 8 + 5 – 4 = 9.$

Accordingly, for the complete combustion of cerium nitrate: glycine mixture, the molar ratio becomes 15/9 = 1.6. The stoichiometric equation for this

$$10Ce(NO_3)_3.6H_2O\,(aq) + 16C_2H_5NO_2\,(aq) \xrightarrow{280^{O}C} 10CeO_2\,(s) + 32CO_2\,(g) + 23N_2\,(g) + 100H_2O\,(g)$$

When the reaction of cerium nitrate and glycine is carried out in the molar ratio of 1: 1.6 the energy released is maximum and the combustion is complete with no carbon residue. This type of stoichiometric balance of a redox mixture for a combustion reaction is fundamental to the synthesis of an oxide material by the solution combustion method [6].

MECHANISM OF COMBUSTION REACTION :

There would be different mechanisms of combustion reaction with different intermediate stages for different oxidizer-fuel combinations; however, a general scheme of mechanism of combustion reaction is presented here.

When a mixture containing oxidizer and fuel with required stoichiometry is heated rapidly at or above the temperature of exothermic decomposition of fuel, initially it undergoes melting and dehydration. Later this mixture foams due to the generation of gaseous decomposition products as intermediates and leads to enormous swelling. The gaseous decomposition products would be a mixture of nitrogen oxides, NH_3, and HNCO. These gases are known to be hypergolic in contact with each other. The foam could be made up of polymers like cyanuric acid, polymeric nitrate, etc., which are combustible. Consequently, the foam breaks out with a flame because of the accumulation of the hypergolic mixture of gases. With an in situ temperature buildup of >1000°C the whole foam further swells and burns with flames. At such high in situ temperature, the foam decomposes to yield 100% product. However, in cases where the gases responsible for combustion are allowed to escape or when their densities are less or the required temperature is not met, combustion does not occur with a flame. The foam only sustains combustion but itself does not initiate ignition. In addition, if the mixture is heated at a slow rate the flame does not appear, since the time required to reach the ignition temperature is longer and all the gases responsible for combustion escape the foam.

THERMODYNAMIC CALCULATION :

Observed high temperature flames during combustion are supported by theoretical calculations of the combustion reaction between oxidizer and fuel based on the heat of formation of reactants and products.

In solution combustion reactions, extremely high temperatures of over 1550°C can be achieved within a very short duration. Therefore, a thermally isolated system exists because there is very little time to disperse the heat to its surroundings. Accordingly, the maximum temperature obtained during the reaction is assumed to be adiabatic temperature (T_{ad}). The heat liberated during the reaction is the enthalpy of the system and is a state function. It is expressed as

$$\Delta H^0 = \int_{298}^{T_{ad}} \Delta C_p(product)dT$$

Where,

n is the number of the moles,

T is the adiabatic flame temperature and

ΔH is enthalpy of combustion, which is given as,

$$\Delta H = \Delta H_{product} - \Delta H_{\mathrm{Re}act\tan t}$$

To determine the theoretical flame temperature, again consider the example of SCS of cerium nitrate to form ceria nano-powders.

Species	ΔH_f (k Cal/mole)	C_p(k Cal/mole k) at 298 k
$Ce(NO_3).6H_2O$	-729.14	-
$C_2H_5NO_2$	-112.2098	-
CeO_2	-260.2	0.01473
N_2	0	0.006798
CO_2	-94.05	0.01115652
H_2O	-57.8	0.0082728

Table 1 : Enthalpy and specific heat at constant pressure of different species involved in stoichiometric combustion reaction of cerium nitrate.

From table 1 and Eq. of ΔH for stoichiometric chemical reaction for SCS of cerium nitrate is,

$\Delta H = -915.408268 - (1159.116) = -243.7077$ Kcal/mole.

Now,

$\sum(nC_p) =$ Summation of specific heats (at constant pressure) of reaction products

Again from table 1,

$\sum(nC_p) = 0.15158$ Kcal/mole K

Solving the Eq. of ΔH^0 for T_{ad}, we get

$$T_{ad} = 298 + \left(\frac{-\Delta H}{\sum(nC_p)} \right) = 1905 \text{ K} = \sim 1600°\text{C}$$

However, the actual flame temperatures will be much lower (±100°C) than the theoretically calculated values, as the radiative losses, incomplete combustion and heating of air may cause the reduction. Despite of these losses, the adiabatic flame temperature at which the reactants are raised during the combustion is much higher than the decomposition temperature (<350°C) of $Ce(NO_3)_3{\cdot}6H_2O$ [6]. Hence, combustion reaction produces the nano-powders despite the short duration (i.e., few seconds) of auto-ignition.

ROLE OF FUELS :

Urea is documented as an ideal fuel for the combustion synthesis of high-temperature oxides like alumina and alkaline earth aluminates. However, a need to employ alternate fuels to prepare oxides, which are unstable above 1000°C such as transition metal aluminates, was necessary. In this regard, hydrazine-based fuels like carbohydrazide (CH), oxalyl dihydrazide (ODH), and malonic dihydrazide (MDH), which have low ignition temperature and are combustible due to the presence of N–N bond that decomposes exothermically to N_2 (N=N) were found to be suitable. Various reported fuels are listed in table 2.

Overall, these fuels serve the following purposes:

1. They are the source of C and H, which on combustion form simple gaseous molecules of CO_2 and H_2O and liberate heat.
2. They form complexes with the metal ions facilitating homogenous mixing of cations in solution.
3. They break down into components from which they are formed. These components in turn decompose to produce combustible gases like HNCO, NH_3 that ignite with NO_x.

Sr. No.	Fuel	Formula	Reducing Valency	Ref.
1.	Urea (U)	CH_4N_2O	+6	Commercially available
2.	Glycine	$C_2H_5NO_2$	+9	
3.	Hexamethylene tetramine (HMT)	$C_gH_{12}N_4$	+36	
4.	Carbo-hydrazide (CH)	CH_6N_4O	+8	[7]
5.	Oxalic acid dihydrazide (ODH)	$C_2H_6N_4O_2$	+10	[8]
6.	Malonic acid dihydrazide (MDH)	$C_3H_8N_4O_2$	+16	[9]
7.	Maleic hydrazide (MH)	$C_4H_4N_2O_2$	+16	[10]
8.	Diformyl hydrazide (DFH)	$C_2H_4N_2O_2$	+8	[11]
9.	Tetraformal Trisazine (TFTA) 4-amino-3,5-dimethyl-l)2,4-triazole	$C_4H_{12}N_6$	+28	[12]

Table 2 : Commonly used fuels in solution combustion synthesis.

Simple compounds such as urea and glycine are recognized as potential fuels. Compounds containing N–N bonds are particularly found to assist the combustion better. Some important criteria that qualify an ideal fuel are:

- Be water-soluble.
- Have low ignition temperature (<500°C).
- Be compatible with metal nitrates, i.e., the combustion reaction should be controlled and smooth and not lead to explosion.
- Evolve large amounts of gases that are of low molecular weight and harmless during combustion.
- Yield no other residual mass except the product oxide.
- Be readily available or easy to prepare.

The type of fuel and the fuel-to-oxidizer ratio influences a combustion synthesis reaction. The exothermic temperature of the redox reaction (T_{ad}) varies from 1000°C to 1500°C. Depending upon the fuel used and the type of metal ion involved, the nature of combustion differs from flaming (gas phase) to non-flaming (smouldering and heterogeneous) type. Flaming reactions could be attributed to the generation of gaseous products like nitrogen oxides (NO_x) by metal nitrates and HNCO, NH_3, CO, etc., generated by fuels.

Theoretically, any redox mixture once ignited, undergoes combustion. All metal nitrates on pyrolysis yield corresponding metal oxides; however, addition of a fuel lowers the decomposition temperature. Hence, the choice of fuel is critical in deciding the exothermicity of the redox reaction between the metal nitrate and the fuel. Depending upon the exothermicity of the reaction, combustion is smoldering, flaming, or explosive. For example, cerium nitrate–glycine reaction is highly exothermic ($T_{ad} \sim 1600°C$) and is explosive. However, if ammonium nitrate is added to above mixture the combustion is much more controlled due to the complex formation of the metal ions.

It is possible to control the particle size of solid combustion product (ash) to nano-range by using suitable fuels that control the nature of combustion. Thus choice of suitable fuel results in,

- Slow burning rate.
- Reduction in exothermicity (making the reaction smoldering instead of flaming, $T_{ad} < 1000°C$).
- Increase in number of gaseous products (water, nitrogen, carbon dioxide, etc.), which

dissipate the heat.

- Linear combustion, which appears to yield nano-oxides unlike volume combustion

CONCLUDING REMARKS :

The exothermicity of the redox chemical reaction in SCS is used to produce useful materials. It has emerged as a viable technique for the preparation of advanced ceramics, catalysts, phosphors, pigments, composites, inter-metallics, and nano-materials.

The salient advantages of SCS process are

- *It is a*n easy and fast process and requires relatively simple equipment.
- Composition, structure, homogeneity, and stoichiometry of the products can be controlled.
- Formation of high-purity products are ensured by this method.
- High exothermicity of the metal nitrate–fuel reaction permits incorporation of desired quantity of impurity ions or dopants in the oxide hosts to prepare industrially useful materials.
- Formation of products of virtually any size (micron to nano) and shape (spherical to hexagonal) can be achieved.
- This method involves lower costs of preparation compared to conventional ceramic methods.
- It is economically attractive and easy to scale up.
- Uniform distribution of the dopants takes place throughout the host material due to the atomic mixing of the reactants in the initial solution.

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