Combustion Synthesized Ceria Powder and its Characterization

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Abstract: Using aqueous combustion synthesis route the ultrafine ceria powder is produced with the help of glycine and nitrate, nitrate utilized as an oxidizer and glycine as a fuel. Using balancing equation with required molar ratios both fuel and oxidizer mixes together in deionized water. Viscous liquids containing glycine and ceric ammonium nitrate gets auto-ignited and resulted in voluminous ceria powder. Characterization is carried out on ceria powder after calcinations process. The resulted powder obtained in the present investigation is in the nano range.

1. Introduction

The production of nano-sized ceramic powders has been the object of growing attention in the last few years. For structural and electrical applications, use as coatings, abrasives, catalyst supports, nanocomposites, and thermal insulators.

Ceria (CeO₂) is a well-known fluorite structured refractory material that can handle oxygen vacancies of both extrinsic and intrinsic and therefore serves as an oxide conducting commodity. Due to the reducing equilibrium regarding Ce³+/Ce⁴+, the intrinsic vacancies are produced by the presence of Ce³+ ions in the lattice. Although extrinsic vacancies are created by the insertion of aliovalent ions in the lattice. In most of its applications, these methods have been widely studied for their large range of fuel cell, sensor and catalytic converter applications. Ceria's special ability to reversibly swapping oxygen is a centre of attention. As illustrated in Equation (1)

\[ \text{CeO}_2-x + \frac{x}{2} \text{O}_2 (g) \rightarrow \text{CeO}_2 \] (1)

Literally, the technology which is performed on a Nano scale is called as Nanotechnology. Nanotechnology has various application in the real world. It bargains with the generation and application of chemical, physical and organic frame works at scales extending from many nanometers to submicron measurements, as well as integration of the coming about nanostructures into bigger frameworks. The nanotechnology incorporates nearly any gadgets or any materials which are organized on the nanometer scale in arrange to perform capacities or get characteristics which might not be something else accomplished.[1-3]
2. Literature review

Nowadays, there are various techniques developed for the synthesis of nanopowders, which are producing very good nanosize powders. These techniques were not applicable for producing nanomaterials. The following are some of the techniques which we come across during synthesis of nanopowders. [4]

2.1. Combustion synthesis

Combustion synthesis (CS) [3-7] has emerged as an important technique for the synthesis and processing of advanced ceramics (structural and functional), catalysts, composites, alloys, inter metallics and nanomaterials. In CS, the exothermicity of the redox (reduction–oxidation or electron transfer) chemical reaction is used to produce useful materials. Depending upon the nature of reactants: elements or compounds (solid, liquid or gas); and the exothermicity (adiabatic temperature, $T_a$), CS is described as: self-propagating high temperature synthesis (SHS); low temperature combustion synthesis (LCS), solution combustion synthesis (SCS), gel-combustion, sol–gel combustion, emulsion combustion, volume combustion (thermal explosion), etc. Combustion synthesis processes are characterized by high-temperatures, fast heating rates and short reaction times. These features make CS an attractive method for the manufacture of technologically useful materials at lower costs compared to conventional ceramic processes. Some other advantages of CS are:

(i) Use of relatively simple equipment
(ii) Formation of high-purity products
(iii) Stabilization of meta stable phases and
(iv) Formation of virtually any size and shape products

2.2. Properties of ceria

- Cerium is a metallic chemical element.
- Cerium is the most reactive & the most abundant rare-earth element.
- Cerium oxidizes rapidly in hot water and slowly in cold water.
- Ceria is used in preparing the lamp mantles and incandescence is formed when burnt out.
- Cerium oxide nanoparticles are very effective in terms of UV filtration.

3. Experimental procedure

Ceric ammonium nitrate [Ce(NO$_3$)$_6$].(NH$_4$)$_2]$ and glycine (NH$_2$CH$_2$COOH) In order to acquire transparent aqueous solutions, a minimum amount of deionized water volume was blended into the necessary molar ratios. These solutions resulted in viscous liquids, hereinafter referred to as precursors, after dehydration has done thermodynamically (at around 80°C on heating stove to extract the surplus solvent). [3]

As soon as viscous-gel obtained, the temperature of the stove is increased to 125°C. These viscous liquids were swelling and igniting instantly at this point, with the rapid evolution to create voluminous powders with a large amount of gases. The self-ignition of the solution accommodating oxidant-to-fuel ratio based on the theory of propellant chemistry, compared to the fuel-deficient precursor, the fuel-rich ratio was known as stronger. In order to eliminate rest of remaining undecomposed glycine, nitrates and their products, the powder produced after auto ignition was calcinated at 500°C up to one hour to obtain uncontaminated, thorough-crystallite cerium oxide (CeO$_2$) powders, because the time for which self-ignition occurs is quite limited (generally ≤ 5 s). For phase detection and crystallite size measurement, X-ray diffraction test was conducted on the produced powders. For a stoichiometric redox reaction, according to the propellant chemistry theory, the ratio of the oxidizing value of nitrate to the reducing value of glycine should be unity between the fuel and the oxidizer. As
gaseous materials, \( N_2, CO_2, \) and \( H_2O \) are usually generated. Therefore, hydrogen and carbon are also considered as elements of reductions.

3.1. Equipments used

- Electrical hot plate.
- Beaker.
- Electronic weighing machine.
- Stirrers.
- Muffle furnace.

3.2. Calcination

This process is going to be carried out in a muffle furnace. It is a process which removes the impurities which were present in the powder. It improves the properties of the powder at higher temperatures. The Muffle furnace temperature range may vary upto 1000\(^\circ\)C. [10-11]

![Figure 3.2.1.Powder obtained before calcination](image1)

![Figure 3.2.2.Powder obtained after calcination](image2)

4. Results and discussion

The essence of a combustion synthesis route and the group potential size calculated on process specifications, such as the fuel type and the fuel to oxidant ratio. These variables specify the temperature at which combustion takes place, the quantity of generated gases and the speed of precursor decomposition. On the higher and lower side of the chemically correct ratio determined by the principle of propellant chemistry, the self-ignition phenomenon occurs for small limits of fuel to oxidant ratios. The ratio well lower than the chemically correct ratio is considered the fuel-deficient ratio, while the fuel-rich ratio is called the ratio higher than the chemically correct ratio. It can be noted that with the fuel-to-oxidant ratio, the flame temperature rises up to a certain range near to flame temperature of the chemically correct ratio.

For the purpose of taking full advantage of the combustion heat and the overall chemical reaction in a one stage, the quantity of fuel usually calculated on the basis of the theory of propellant chemistry. In the event of a chemically correct redox reaction between an oxidizer and fuel. Unity should be the ratio of the net oxidizing and declining valence of the metal nitrates to the total declining valence of the fuel. Using the valencies of individual elements, the net oxidizer and declining valencies of metal nitrates and fuel can be calculated. Oxidizer and reduction valencies are determined by taking element valencies as +4 for Ce, +4 for C, +1 H, -2 for FIR, and zero for N, respectively. The idealized reaction that could happened during the synthesis of a ceria powder with ceric ammonium nitrate as an oxidizer and the glycine as fuel is given below, according to the propellant chemistry:
\[
\text{Ce(NO}_3\text{)}_6\text{(NH}_4\text{)}_2 + \frac{8}{3} \text{NH}_2\text{CH}_2\text{COOH} \rightarrow \text{CeO}_2^{2+} + \frac{32}{3} \text{H}_2\text{O} + \frac{16}{3} \text{CO}_2 + \frac{16}{3} \text{N}_2
\]

Hence, in order to synthesis 1 mole of CeO\(_2\) powder through stoichiometric redox reaction = 2.66 moles of glycine required. Therefore, the glycine-to-nitrate ratio for the reaction is equal to 0.44. Studies on combustion synthesis route using glycine as fuel shows that the ratios of fuel rich and stoichiometric fuel will result in uncontrollable combustion due to the increased temperature of the flame accompanied with the rapid decomposition of the precursor.

![Figure 4.1. cerium oxide X-RD graph](image1)

![Figure 4.2. SEM image of ceria powder at 500°C](image2)

![Figure 4.3. SEM image of ceria powder at 700°C](image3)
5. Conclusion

The following conclusions are drawn from the present works:

1. Nano crystalline cerium oxide powders having scale of crystallite in the array of 15-40 nm are successfully synthesized using combustion synthesis route.
2. SEM analysis is carried out to analyse morphology of ceria powder.
3. Even though producing nanocrystalline, compositionally homogeneous powders, the aqueous combustion synthesis route is inexpensive and simple to conduct.
4. The process has a high degree of producibility and a strong promising method for sinter-active nanocrystalline cerium to be generated on a large scale.
5. This technique is simple, fast and single step process.

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