

SOLUTION COMBUSTION SYNTHESIS OF NANOSCALE OXIDES AND THEIR COMPOSITES

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Abstract. Nanosize alumina, ceria, yttria, zirconia $\text{CeO}_2\text{-ZrO}_2$ (OSC), $\text{t-ZrO}_2\text{-Al}_2\text{O}_3$ (ZTA) and $\text{Y}_2\text{O}_3\text{-ZrO}_2$ (YSZ) have been prepared by the combustion of aqueous solutions containing corresponding metal nitrate, ammonium nitrate and glycine redox mixtures. The combustion is non-flaming (smoldering) and yields voluminous oxides with large surface area ($10\text{-}30\text{ m}^2\text{g}^{-1}$) and nanosize ($10\text{-}50\text{ nm}$). Powder XRD and TEM have been used to characterize the products of combustion.

1. INTRODUCTION

"Nanomaterials" possessing 1-100 nm grain sizes have unique chemical, physical, optical and mechanical properties. Because of these properties, they are useful as sensors, catalysts, coating materials (modifiers of surface properties) and miniaturization of devices (IC chips) [1]. For example, nanosize alumina or ceria having large surface/volume ratio are used as catalyst supports, $\text{t-ZrO}_2\text{-Al}_2\text{O}_3$ is a well known toughened ceramic (ZTA) [2], yttria stabilized zirconia (YSZ) is a solid electrolyte [3] and $\text{CeO}_2\text{-ZrO}_2$ oxygen storage capacitor (OSC) [4]. The dispersion of nanoparticles in various fluids allows the preparation of magnetic fluids ($\gamma\text{-Fe}_2\text{O}_3$), fabrication of thin film (sensors) and antireflection / antifogging coatings (TiO_2) or improvements of optical properties [5].

Various techniques are available for the preparation of nanomaterials. They include dividing or breaking down a bulk solid or building up processes. Some of the well-known methods are: laser abrasion, plasma synthesis, chemical vapor deposition, mechanical alloying or high-energy milling and sol-gel synthesis [6]. All these techniques are involved, require special chemicals and equipments. During the course of our studies, we have prepared a variety of oxide materials by the low temperature initi-

ated, self-propagating, gas producing combustion method [7-10].

Here, we describe a simple solution combustion method for the preparation of nanosize alumina, ceria, yttria, zirconia, $\text{CeO}_2\text{-ZrO}_2$, $\text{t-ZrO}_2\text{-Al}_2\text{O}_3$ and $\text{Y}_2\text{O}_3\text{-ZrO}_2$ etc. using corresponding metal nitrate, ammonium nitrate and glycine redox mixtures. The process is fast (instantaneous) and yields high purity, homogenous crystalline products with desired composition and structure.

2. EXPERIMENTAL

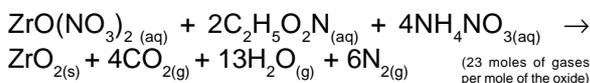
Nanosize alumina, ceria, yttria, zirconia and their composites were synthesized by the combustion of aqueous solutions containing stoichiometric amounts of the corresponding metal nitrate (Glaxo), ammonium nitrate (Qualigens) and glycine (Merck). Stoichiometric composition of the redox mixture was calculated based on the total oxidizing and reducing valencies of the oxidizer and the fuel keeping the O/F ratio unity [11]. The aqueous solution containing the redox mixture in a Pyrex container when introduced in a muffle furnace preheated to $400\text{ }^\circ\text{C}$, boils, foams and undergoes smoldering (flameless) combustion to produce the corresponding oxides. The product left behind is voluminous and erupts like a volcano as shown in Fig. 1.



Fig. 1. Formation of voluminous zirconia.

The combustion can also be initiated using a kitchen microwave oven (IFB, 750 W, 2.45 GHz, 1.2 ft³). The time taken in the microwave preparation is much shorter than that of the furnace method. The products of combustion are similarly voluminous and fluffy.

Assuming complete combustion, the theoretical equation for the formation of zirconia with glycine can be written as follows:



Similar equations can be written for the formation of other oxide materials.

Powder XRD, SEM, TEM, and surface area and density measurements have been used to characterize the products of combustion. Powder X-ray diffraction measurements were made on a Shimadzu XD-DI Diffractometer using nickel-filtered Cu K_α radiation. SEM micrographs were recorded from a Jeol JSM-840A instrument after coating the samples with gold. TEM images were obtained from a Jeol (JEM 200CX) microscope operated at 200 kV, by depositing the methanolic suspension of the powder on

carbon-coated copper grids. Surface area and pore volume measurement were done using the nitrogen gas adsorption multipoint BET method (Model 2100E Accusorb, Micrometrics Instrument) assuming a cross-sectional area of 0.162 nm² for the nitrogen molecule. Powder density was measured using a pycnometer with xylene as the liquid medium.

3. RESULTS

The XRD's of the various oxides are shown in Fig. 2. It is interesting to note that the as prepared oxides are all crystalline and the lattice constants calculated are in agreement with the literature. The TEM image of as synthesized zirconia and a nano-nano composite of CeO₂-ZrO₂ are shown in Fig. 3. and 4 respectively.

Some of the particulate properties of these oxides are summarized below and in Table 1. The powders are fluffy and fine as seen by their density and surface area data.

Alumina: α – alumina prepared by the urea-nitrate mixture is usually micron size with hexagonal geometry of the particles. In the glycine fuel method, although the flame temperature is much lower (<1000 °C), the product is crystalline with the formation of the stable alpha phase. The particles are in the size range of 40 – 60 nm with spherical to acicular in shape. The surface area of the oxide prepared by glycine (14 m²g⁻¹) is higher than that produced by the urea method (8 m²g⁻¹). The preparation of alumina by the glycine method requires extra oxidizer (NH₄NO₃) than the stoichiometry.

Ceria: Ceria formed by the combustion of glycine mixture is cubic in nature with a surface area of (30 m²g⁻¹) and particle size 20-30 nm. The particles are mostly spherical in shape.

Yttria: Yttria is also cubic in nature. TEM micrographs show the particles to range from 15 – 25 nm that have hexagonal to spherical shape. The surface area of this oxide is higher than that produced by other fuels for combustion.

Table 1. Particulate properties of the nano-oxides.

Oxides	Tap density (gm.cm ³)	Powder density (gm.cm ³)	BET surface area (m ² g ⁻¹)	Particle size From TEM (nm)
Al ₂ O ₃	0.23	3.1	14	55
CeO ₂	0.16	1.8	30	15
Y ₂ O ₃	0.25	2.2	33	40
ZrO ₂	0.18	2.8	17	20

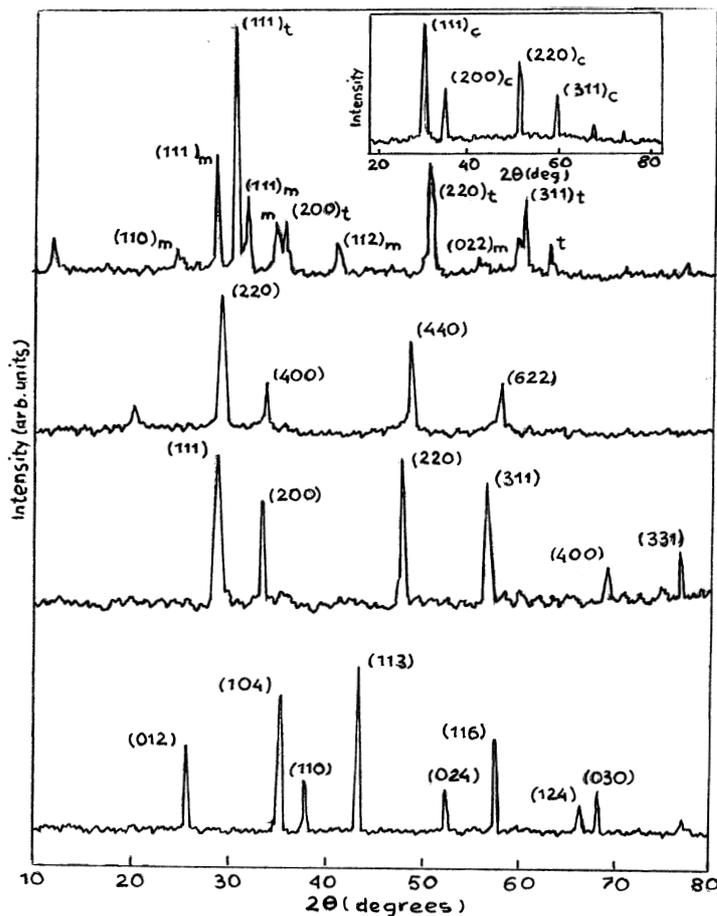


Fig. 2. XRD pattern of (a) α - Al_2O_3 (b) CeO_2 (c) Y_2O_3 (d) mt-ZrO_2 inset $5\% \text{Y}_2\text{O}_3/\text{ZrO}_2$.

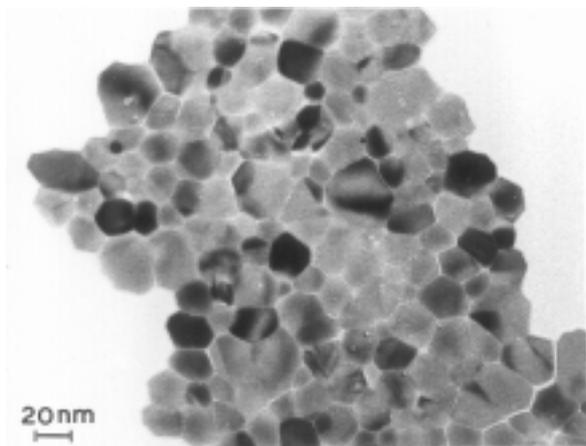


Fig. 3. TEM photograph of ZrO_2 .

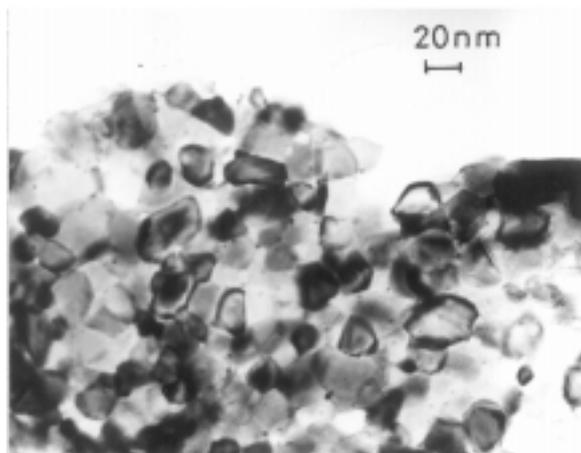


Fig. 4. TEM photograph of CeO_2 - ZrO_2 .

Zirconia: The as-formed zirconia is a mixture of both tetragonal and monoclinic (mt) phases. The metastable tetragonal phase containing partially monoclinic feature is easily stabilized to the cubic phase by the addition of (5%) ceria or yttria (Fig. 2 inset). The TEM photograph of zirconia shows a

uniform and compact distribution of the particles. The particles show a nearly spherical to hexagonal geometry with ≤ 20 nm size. It appears that the particles are dispersed with negligible agglomeration and show higher surface area.

Nanocomposites: Composites of zirconia like CeO_2 - ZrO_2 , t-ZrO_2 - Al_2O_3 and Y_2O_3 - ZrO_2 have also been prepared by this single step method. Addition of ceria or yttria stabilizes the metastable (mt) zirconia phase to cubic. These composites can be sintered at much lower temperatures of 1000-1200 °C.

4. CONCLUSIONS

The glycine fuel method appears to be well suited for the preparation of nano size zirconia and its composites. Some of the salient features of the process are:

- The oxides and their composites can be prepared at very low temperatures of < 400 °C;
- The products are homogenous and crystalline;
- They are soft and fine with high surface area;
- The materials prepared are of high purity (99.99%);
- The particles show less agglomeration and can be directly used as coatings;
- Large quantities can be prepared relatively cheaply.

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