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Nanocrystalline ceria from carbon free materials

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Abstract

Nanocrystalline ceria powders were synthesized using carbon free starting materials, viz. $Ce(NO_3)_3{\cdot}6H_2O$, hydrazine and ammonium nitrate. Thermal decomposition of the precursors was studied by TG-DTA. The powders obtained in both the cases have crystallite size of about 13 nm, as calculated by X-ray line broadening, and a high surface area of $>75\ m^2/g$. The deagglomeration behaviour was also investigated, by dynamic light scattering experiments, for the two powders to ascertain the nature of agglomerates. The sintered density of the powders after sintering in air at 1250 °C for 2 h was found to be about 94% and 90%, respectively, of the theoretical density, for hydrazine and ammonium nitrate derived products.

Keywords: A. Calcination; B. Grain size; D. CeO_2

1. Introduction

Ceria has attracted a considerable interest in recent years due to its diverse applications. It acts as a three ways catalyst for automobile exhaust emission control [1]. CeO_2 is also a candidate material for variety of potential applications e.g. optical glass-polishing, petroleum-cracking catalyst, a gas sensor [2]. A variety of these applications need powders in the nanocrystalline form. The nano-particles, in general, show higher catalytic activity, better sinterability and other unusual properties in contrast to the bulk materials [3]. The synthesis of nanostructured ceria powder with controlled powder characteristics is of practical importance to get dense sintered product at a lower sintering temperature, in particular when problem of change of valence state of cerium ($Ce^{4+} \rightarrow Ce^{3+}$) is associated during sintering at higher temperature (>1300 °C) [4].

Nanocrystalline ceria powder has been reported to be synthesized by different techniques including hydrothermal [5], precipitation [6], electrochemical [7] and combustion [8,9]. Different sintering behaviours have been observed for ceria powders prepared by these different routes [5–11]. These wet chemical processes provide an intimate blending among the constituents. Therefore, the phase pure materials with improved powder characteristics can be obtained at a much lower calcination temperature. In many of these processes, various decomposition products are also incorporated in the final product. An additional step of calcination at higher temperatures has to be, therefore, added to get rid of these undesired products. Mostly in the combustion synthesis carbon containing fuels are used, which often leads to leftover carbon in the final product. Another serious problem arises when carbonates are formed instead of oxides, due to the reaction of precursors with CO_2 generated out of combustion of fuels. This problem is more aggravated while dealing with two or more component system [12] as one needs higher calcination temperatures to decompose these carbonates, which deteriorates the powder properties. In order to circumvent these problems, we have tried to synthesize ceria powders free of any carbon impurity, by using non-carbon containing precursors. The starting materials (free from any carbon) chosen for this purpose was commonly available ammonium nitrate. Another carbon free material, viz. hydrazine was used as a reference for the

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comparison of the powder properties obtained from the two materials. The hydrazine method was already used by Nakane et al. [11]. Also, in all the previous work on nanocrystalline ceria, there is no mention on the nature of the agglomerates. The extent and nature of the agglomerates (soft or hard) has a strong bearing on sinterability and other related powder properties. Therefore, the deagglomeration behaviour for the two powders was investigated using a particle size analyzer. The effect of decomposition steps of the two precursors was also investigated, as it seems to govern the properties of the final products. The precursors were analyzed by TG-DTA for understanding the decomposition process. The subsequent powders obtained were characterized by XRD, surface area analysis, sinterability, and their microstructures were studied by SEM.

2. Experimental

AR grades of cerium nitrate $Ce(NO_3)_3 \cdot 6H_2O$, hydrazine hydrate and ammonium nitrate were used as the starting materials. A clear solution of cerium nitrate was mixed with a solution of 80% aqueous hydrazine till complete precipitation occurs. The precipitate separated out was filtered and washed thoroughly to remove any adsorbed hydrazine or nitrate ions. The dried precipitate was used as the precursor for the final product. The precursor was analyzed by TG-DTA to study the decomposition behaviour. It was then further heated at $\approx$300 °C, giving rise to fine ceria powders accompanied by a mild gaseous evolution during the decomposition process.

Another solution of cerium nitrate with ammonium nitrate was prepared in the molar ratio 1:1. In case of ammonium nitrate a transparent aqueous solution was obtained which on thermal dehydration at about 80 °C gave rise to a gel. The dried gel was analyzed by TG-DTA. The gel obtained was then further heated at about 300 °C to give nanocrystalline ceria powders. In this case however, a vigorous gaseous evolution and frothing of the gel was observed during the decomposition process.

TG-DTA was carried on an SETARAM instrument (92-16.38 model) at a heating rate of 10 °C/min in air, from room temperature to 800 °C. The powders obtained from both the precursors were calcined further at 500 °C for removing traces of nitrates, if any, and to obtain well crystalline ceria powders. Both the calcined and uncalcined powders were analyzed for the presence of nitrates, if any. X-ray diffraction was carried on the combustion synthesized powders for phase identification and the crystallite size estimation, using Cu Kα radiation on a Philips X-ray diffractometer, Model PW 1927. Silicon was used as an external standard for correction due to instrumental broadening. The surface area analysis of the ceria powders was carried out by standard Brunauer–Emmett–Teller (BET) technique with N_2 adsorption using a Sorptomatic 1990 CE instrument. The ceria powders obtained from both the precursors were cold pressed in the form of the 12 mm diameter pellets at a compaction pressure of 200 MPa using a uni-axial hydraulic press. Stearic acid was used as a lubricant. Sintering was performed in air at 1250 °C for 2 h with a heating rate of 10 °C/min. The sintered densities were determined using the Archemedes' principle. The extent and nature of agglomeration was studied by a particle size analyzer. The equipment used was Horiba, Model LA-500 (Japan), particle size analyzer based on laser diffraction, which covers the particle size range of 0.20–200 μm. The microstructure studies on the sintered pellets were carried out by scanning electron microscopy, using a Jeol Scanning Microscope, Model JSM-T330A. The sintered pellets were copper coated before SEM studies.

3. Results and discussion

TG-DTA was performed on both the dried precursors to ascertain the final decomposition temperature. The TG-DTA curve of the dried hydrazine precursor (Fig. 1a), shows a gradual weight loss occurring till 200 °C which is associated with endotherms near 100 °C, probably corresponding to the loss of water. The weight loss up to this step is only about 35%. No further weight loss was observed on further heating till 800 °C. The TG-DTA curve of the ammonium nitrate

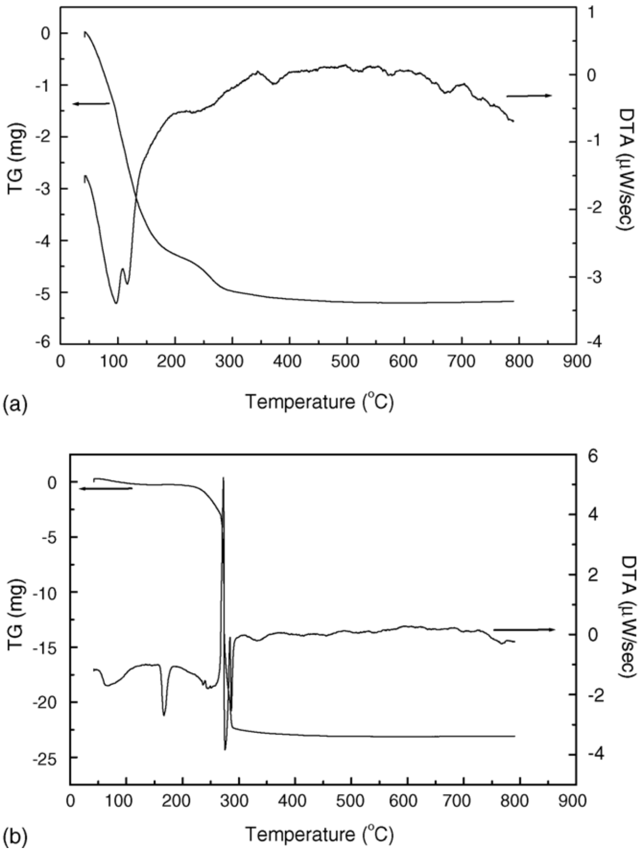

Fig. 1. TG-DTA of dried precursors: (a) hydrazine precursor, (b) NH_4NO_3 precursor.

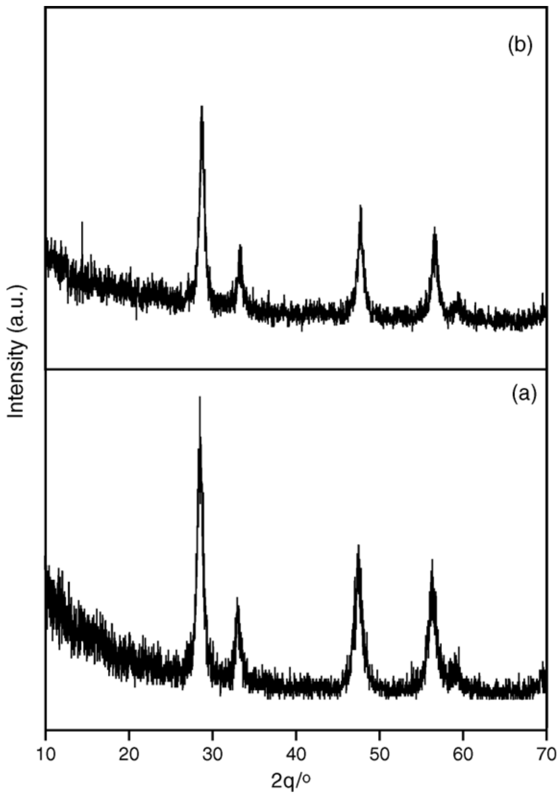

Fig. 2. XRD patterns of powder after calcination at 500 °C: (a) NH_4NO_3-derived product, (b) hydrazine-derived product.

precursor is shown in Fig. 1b. Here a sharp exothermic peak is observed at about 270 °C and the decomposition is complete in a single step at this temperature unlike the previous case, where it is a prolonged process. The weight loss corresponding to this step is about 65%. An endothermic peak is observed at about 170 °C probably corresponding to loss of water of crystallization. No further weight loss or DTA peaks were observed till 800 °C. Thus, in this case it was decided to heat the precursor at a minimum temperature of about 270 °C for complete decomposition to give the final product.

Nitrogen contents of the ceria powders obtained from both fuels were carried out using elemental analysis. The nitrogen content was less than 0.5% for uncalcined powders as well as for the powders that were calcined at 500 °C for 1 h. Thus indicating that all nitrogen is lost during the decomposition process itself. The powders obtained after calcination at 500 °C were characterized by XRD. The XRD patterns of the two calcined powders are given in Fig. 2a and b both confirming the F-type cubic phase of CeO_2. The crystallite size of the powders was calculated from X-ray line broadening. The crystallite size for the powders calcined at 500 °C for 1hr was approximately 13 nm for both the cases. Thus, the two powders seem to be identical considering their crystallite sizes.

The ceria powders obtained in both cases showed very high surface areas. The ceria powders after calcination at 500 °C, synthesized from hydrazine had a surface area of about 50 m^2/g while that from ammonium nitrate had a surface area of about 73 m^2/g. The surface areas for the uncalcined powders were found to be as high 75 and 87 m^2/g as obtained from hydrazine and ammonium nitrate, respectively. The high surface area could be attributed to the frothing due to the evolution of gases that are liberated as the decomposition products. The TG curve suggests that the percentage weight loss in case of ammonium nitrate is more (65%) than that compared to hydrazine (35%) precursor. Thus, the nature of decomposition of precursor and gas evolution during this process seem to govern the powder characteristics like surface area, crystallite size, extent of agglomeration and in turn sinterability as discussed later. It could be noted that similar results were also obtained for the combustion synthesized ceria powders [9]. Thus, if the gel/precursor decomposes in a single step, it is supposedly a better situation for the low temperature synthesis with improved powder characteristics because in this case all the gaseous products are evolved at the same time so that the premature local partial sintering among the primary crystallites can be minimized. This trend in surface area was further supported by the deagglomeration studies explained below.

Extent and nature of agglomeration in the powder after calcination at 500 °C was studied by a particle size analyzer based on laser diffraction. The technique is used as an indication for particle size distribution of powders. However, the success of the technique depends on dispersion of the powder. Since the synthesized powders are essentially agglomerates of primary nanoparticles, it is difficult to disperse them as individual particles and hence in spite of true particle size the results are merely indicative of size of agglomerates. However, due to instrumental limitation, the particle size distribution analyzer based on laser diffraction is not capable of giving the true size of the nanaoparticles but it is good tool to find out the size of agglomerates. In order to have a feeling of the extent and nature of agglomeration, the particle size distribution of the powder has been measured before and after ultrasonic treatment. Figs. 3a and b and 4a and b show the particle size distribution of the powder before (a) and after (b) ultrasonic treatment, prepared using hydrazine and ammonium nitrate, respectively. Fig. 3a suggests the presence of two types of agglomerates. A majority of the agglomerates covered a very wide range from 5 to 100 μm, with highest concentration in the range of 20–30 μm. Also a small portion of particles, which were less than 1 μm in size were found to be present. Fig. 3b shows the size distribution after ultrasonication for a period of 10 min. In this case, the two kinds of particle size distributions were clearly observed, indicating the presence of two types of agglomerates. Thus there were more number of particles with average size of less than 1 μm compared to that present before ultrasonication in the earlier case. Also the median shifted from 25 μm to about 10 μm for that of the majority particles. Thus it could be suggested that majority of the

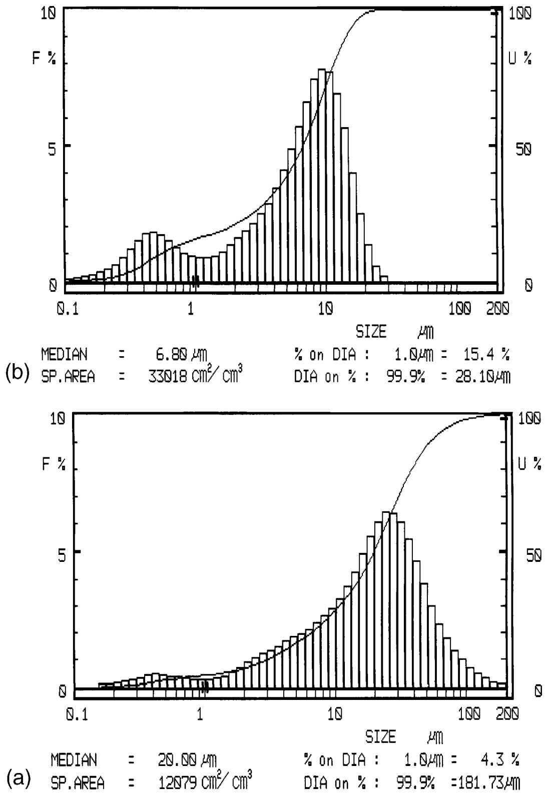

Fig. 3. Deagglomeration behaviour in powders using hydrazine: (a) before ultrasonication, (b) after ultrasonication.

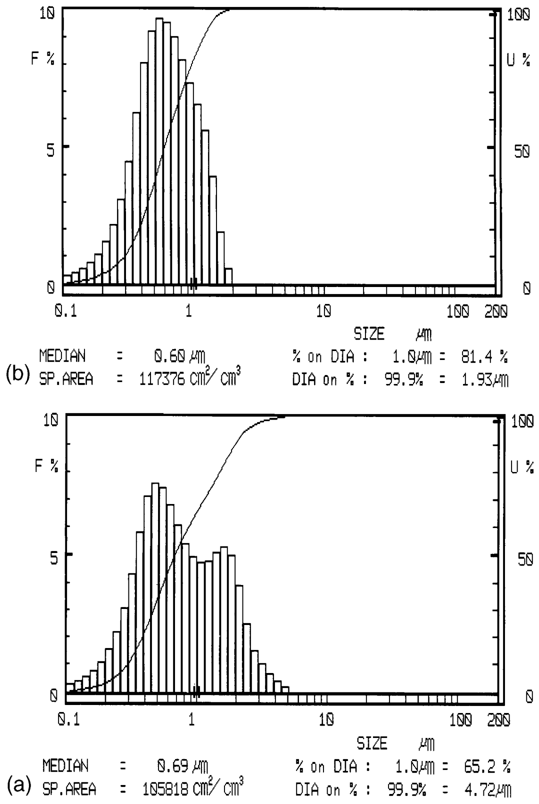

Fig. 4. Deagglomeration behaviour in powders using ammonium nitrate: (a) before ultrasonication, (b) after ultrasonication.

agglomerates are relatively hard in nature as the average agglomerate size remained on the higher side of about 10 µm even after ultrasonication. Also a small portion of soft agglomerates (less than 1 µm). was found to be present. Fig. 4a shows the graphs for powders obtained using ammonium nitrate without any ultrasonication. In this case the size distribution was found to be of a much narrower range from 0.2 to 5 µm. Fig. 4b shows the distribution after ultarsonication for 10 min. A drastic reduction in size distribution and average size was observed. Thus, essentially all the particles on ultrasonication were reduced to less than 1 µm. Thus, in this case it can be inferred that these agglomerates are basically soft in nature and could be easily broken down by mere ultrasonic treatment. The particle sizes that are shown in these figures are in fact the size of the agglomerates of the nanoparticles, which are loosely bound in these agglomerates. Thus, the deagglomeration studies are in agreement with the surface area results, suggesting that the evolution of gases that are liberated in the form of the decomposition products are crucial for controlling the final powder properties.

These powders after calcination at 500 °C were sintered at 1250 °C for 2 h. The sintered densities as measured by Archemedes' principle were found to be 94% and 90% of the theoretical densities, for hydrazine and ammonium nitrate, respectively. SEM studies were carried on the well-sintered pellets. Fig. 5a shows the SEM micrographs of the powders obtained from NH_4NO_3 and Fig. 5b for that obtained from NH_2NH_2. The micrographs for Fig. 5a contain grains that are essentially spherical and lie in the range 0.5–1.0 µm. In Fig. 5b the grains are much larger with an average grain size of about 2–2.5 µm. Thus, fine grain microstructure is obtained even after sintering, as sintering was carried out for shorter durations of just 2 h, by avoiding considerable grain growth. Thus, the ultrafine nature and high surface area of the starting powder seems to be responsible for producing high sintered density at a low temperature in shorter duration. Although there is not a major difference in the densities, the hydrazine-derived product shows comparatively better density as also evident from the micrographs. It is known that high sintered densities are observed from powders consisting of unit particles with high density and also high surface area [13]. Like wise, in case of ceria by Nakane et al. [11] the powders that are calcined at temperatures of about 700–800 °C give better density than those of powders that are calcined at lower temperatures or at higher temperatures. Thus, there is an optimum value for calcination of the powders prior to sintering. The primary units in hydrazine-derived particles may be having higher density as compared to that of ammonium nitrate. Also the relative higher surface area in the case of ceria powders obtained from NH_4NO_3 may be responsible for having smaller grains as compared to that obtained from NH_2NH_2, though the density was greater in the case of hydrazine derived powders.

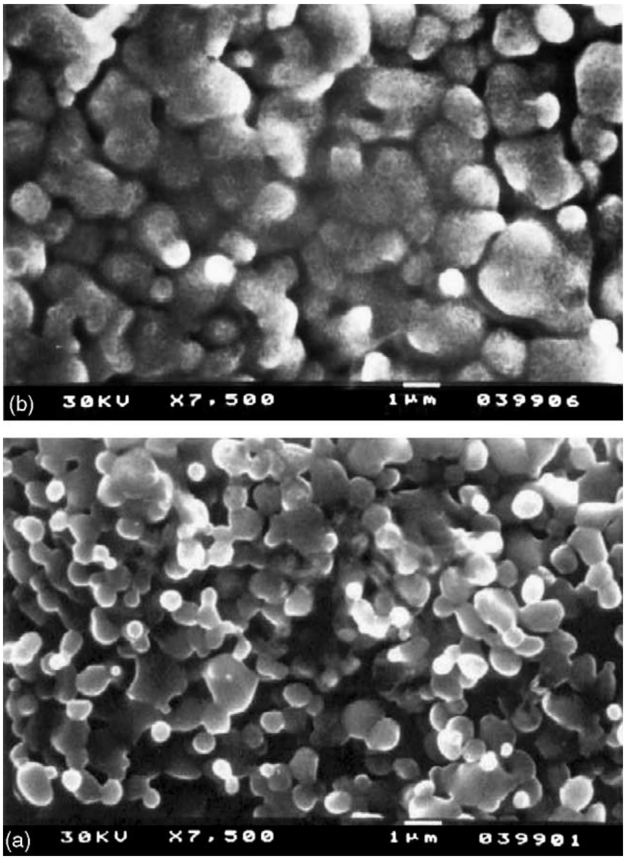

Fig. 5. SEM micrograph showing microstructure of sintered pellet: (a) NH_4NO_3-derived product, (b) hydrazine-derived product.

4. Conclusions

Nanocrystalline ceria powders could be synthesized in a simplified manner from common carbon free materials. The effect of the nature of the two precursors used here, on the powder characteristics was studied. It is found that both hydrazine and ammonium nitrate can be successfully used for synthesizing carbon free nanocrystalline ceria powders. The powder prepared from ammonium nitrate was found to consist of soft agglometates, which could be broken down by mere ultrasonication. It also appears that ammonium nitrate can be more effective as a precursor for preparing nanoceramics with appreciable powder properties.

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