

Combustion synthesis of fine-particle ceria

M. MARIA AMALA SEKAR, S. SUNDAR MANOHARAN, K. C. PATIL

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India

Fine-particle ceria having narrow size distribution is of interest as polishing material for ophthalmological lenses, television tubes, plates and mirrors [1]. The preparation has been reported of such ceria by the hydrolysis of cerium isopropoxide [2] and cerium nitrate [3, 4] followed by thermal decomposition, as well as by the thermal decomposition of cerium oxalate hydrazinate [5] and cerium hydrazine carboxylate [6]. In this letter we report the preparation of fine-particle, large-surface-area ceria by the combustion process developed for the preparation of α -alumina [7], aluminates [8], chromites [9] and ferrites [10]. The process involves rapid decomposition of a saturated aqueous solution containing ceric ammonium nitrate and urea ($\text{CH}_4\text{N}_2\text{O}$), carbonylhydrazide ($\text{CH}_6\text{N}_4\text{O}$ (CH)), oxalyl dihydrazide ($\text{C}_2\text{H}_6\text{N}_4\text{O}_2$ (ODH)) or tetraformal trisazine ($\text{C}_4\text{H}_{16}\text{N}_6\text{O}_2$ (TFTA)) redox mixtures.

Cerium oxalate hydrate ($\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$), cerium oxalate hydrazine hydrate ($\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 3\text{N}_2\text{H}_4 \cdot 11\text{H}_2\text{O}$) and cerium hydrazine carboxylate ($\text{Ce}(\text{N}_2\text{H}_3\text{COO})_3 \cdot 3\text{H}_2\text{O}$) were prepared as reported in [5, 6]. Stoichiometric compositions of ceric ammonium nitrate with various fuels were calculated using the total oxidizing and reducing valencies of the compounds which serve as numerical coefficients for stoichiometric balance so that the equivalent ratio Φ was unity and the energy released by the combustion was at a maximum [11]. The actual weights of redox compounds and the mixtures used for combustion are given in Table I. The combustion of redox compounds and mixtures dissolved in the minimum quantity of water was carried out in a cylindrical Pyrex dish of capacity 300 cm^3 by introducing it into a furnace maintained at $350 \pm 10^\circ\text{C}$.

The products obtained from the combustion were characterized by X-ray diffraction (XRD) patterns (Fig. 1) recorded using a Philips PW 1050/70 X-ray

diffractometer and $\text{Co-K}\alpha$ radiation. The powder densities were measured using a pycnometer in xylene medium. Particle size measurements were carried out using a micrometre photo size (model SKC 2000) and the surface areas of ceria were measured by nitrogen adsorption employing a Micromeritics Accusorb 2100E instrument.

Most cerium salts containing oxidizing anions decompose to cerium dioxide on heating. The decomposition temperature of the salts can be lowered by incorporating reducing groups. Thus, ceric ammonium nitrate, which contains NH_4^+ ion, decomposes in the range 220 to 260°C , compared with $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ which decomposes in the temperature range 230 to 360°C [12] to yield CeO_2 . The surface area and particle size of ceria obtained by combustion of ceric ammonium nitrate at 350°C are $14.0\text{ m}^2\text{ g}^{-1}$ and $1.6\ \mu\text{m}$, respectively, and has 58% theoretical density. The low surface area and large particle size of CeO_2 obtained by the thermal decomposition of ceric ammonium nitrate compared with $90\text{ m}^2\text{ g}^{-1}$ obtained from cerium hydrazine carboxylate could be attributed to the rapid decomposition of the former. It is possible to increase the surface area of ceria and hence obtain fine particles with narrow size distribution by controlling the combustion process. This has been achieved by using different fuels in the redox mixture. The main feature of the fuels being that (1) they are all hydrazine based and therefore contain a potent N-N bond (e.g. CH, ODH and TFTA) and (2) they are water-soluble and combustible with low ignition temperature. The particulate properties of ceria such as the density, surface area and particle size are summarized in Table I. The results are compared with those of ceric ammonium nitrate, cerium oxalate hydrate, hydrazinate and hydrazine carboxylate. It is interesting to see that ceria obtained has 53 to 60% theoretical density with surface area ranging from

TABLE I Composition of redox compounds or mixtures and their combustion product (ceria)

Sample No.	Composition of redox compound or mixture	Properties of ceria			
		Density (g cm^{-3} (% theoretical*))	Surface area ($\text{m}^2\text{ g}^{-1}$)	Particle size from surface area (μm)	Average agglomerate size (μm) [†]
1	$\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$ (10 g)	4.3 (60)	43.0	0.031	0.71
2	$\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 3\text{N}_2\text{H}_4 \cdot 11\text{H}_2\text{O}$ (10 g)	4.0 (56)	70.0	0.022	0.87
3	$\text{Ce}(\text{N}_2\text{H}_3\text{COO})_3 \cdot 3\text{H}_2\text{O}$ (10 g)	3.8 (53)	90.0	0.017	0.76
4	$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ (10 g)	4.1 (58)	14.0	0.105	1.60
5	$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ (10 g) + $\text{C}_4\text{H}_{16}\text{N}_6\text{O}_2$ (2.9 g)	4.0 (56)	52.0	0.029	1.28
6	$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ (10 g) + $\text{CH}_6\text{N}_4\text{O}$ (3.4 g)	3.9 (54)	65.0	0.027	0.94
7	$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ (6.8 g) + $\text{CH}_4\text{N}_2\text{O}$ (2.6 g)	3.9 (54)	84.0	0.019	0.88
8	$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ (6.8 g) + $\text{C}_2\text{H}_6\text{N}_4\text{O}_2$ (3.5 g)	3.9 (54)	85.0	0.018	0.61

* 7.13 g cm^{-3} ; [†]From sedimentation method.

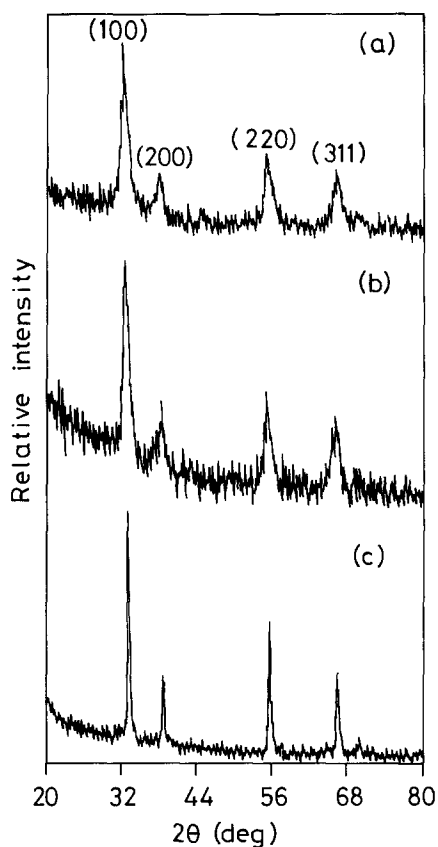


Figure 1 XRD pattern of ceria obtained from (a) cerium hydrazine carboxylate, (b) ceric ammonium nitrate with ODH and (c) ceric ammonium nitrate.

40 to $90 \text{ m}^2 \text{ g}^{-1}$ compared with $14 \text{ m}^2 \text{ g}^{-1}$ for ceric ammonium nitrate. The surface area of ceria shows an increase by an order of 4 to 6. The particle size of ceria calculated from surface area varied from 0.017 to $0.03 \mu\text{m}$. Fine particle nature of ceria is also reflected in the X-ray line broadening (Fig. 1). Typical histograms of ceria obtained from the combustion of redox mixtures are shown in Fig. 2. It can be seen that 80% of the particles are below $10 \mu\text{m}$ with the average agglomerate size of CeO_2 varying from 0.61 to $1.28 \mu\text{m}$.

The observed dramatic change in the particle size and the surface area of ceria may be attributed to the nature of combustion of ceric ammonium nitrate in the presence of fuels. The redox reaction is highly exothermic and is accompanied by the evolution of gases like nitrogen, H_2O and CO_2 . The evolution of gases helps not only to disintegrate the product but also to dissipate the heat of combustion, thus inhibiting sintering. The observed variation in the surface area of CeO_2 with different fuels may be attributed to the number of moles of gases evolved, the burning rate and the combustion time. Fuel-rich precursors such as cerium oxalate, hydrazinate and hydrazine carboxylate which decompose or combust using atmospheric oxygen at low temperatures (240 to 300°C) appear to yield fine-particle ceria. This may be due to the low ignition temperature, slow burning and the evolution of a large amount of gases.

In conclusion, it has been possible to obtain fine-particle (0.017 to $0.1 \mu\text{m}$) and large-surface-area (43 to

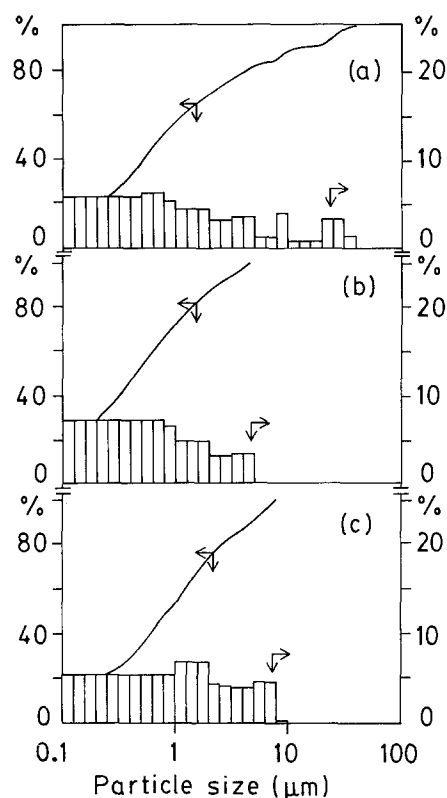


Figure 2 Particle size distribution curves of ceria obtained from (a) cerium hydrazine carboxylate, (b) ceric ammonium nitrate with ODH and (c) ceric ammonium nitrate.

$90 \text{ m}^2 \text{ g}^{-1}$) ceria by the combustion of appropriate redox compounds or mixtures.

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