Combustion Synthesis and Characterization of Nanocrystalline CeO_2-Based Powders

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Nanocrystalline cerium oxide based powders (CeO_2, $(GdO_{1.5})_{0.2}(CeO_2)_{0.8}$, and $(SmO_{1.5})_{0.2}(CeO_2)_{0.8}$) have been produced using combustion synthesis with glycine as fuel and nitrate as oxidizer. The pure CeO_2 powders prepared by using different glycine-to-nitrate ratios have been characterized by X-ray diffraction (crystallite size), thermogravimetry, infrared spectroscopy, surface area analysis, and transmission electron microscopy. The influence of calcination temperature on crystallite size, surface area, and carbonate species remaining from the combustion reaction has been studied especially for the near stoichiometric glycine/nitrate ratio (G/N = 0.55) to reveal the optimal synthesis conditions for all three compositions. A G/N ratio of 0.55 and calcination at 550 °C in oxygen flow gave high quality powder with a crystallite size of ∼10 nm. The powders had excellent sintering properties with an onset of densification at ∼600 °C.

Introduction

Cerium oxide (CeO_2)-based ceramic materials can be rendered ionic conducting, electronically conducting, or mixed conducting dependent on substitution, temperature, and partial pressure of oxygen. Due to this possibility to tailor the electrical behavior, CeO_2-based materials have attracted much attention for applications such as solid electrolytes for solid oxide fuel cells (SOFC),[1] catalysts for automotive exhaust treatment,[2] oxygen sensors,[3] and petroleum cracking catalysts. CeO_2-based electrolytes have a higher ionic conductivity compared to the traditionally more frequently used ZrO_2-based materials[4] which means that devices with CeO_2-based materials can be operated at a lower temperature. At present there is considerable interest in increasing the ionic conductivity of these materials by decreasing the grain size into the nanometer range.[5] Since grain boundaries possess high defect densities and high mobilities, which are the two most important factors for increased ionic conductivity, the ionic conductivity may be significantly enhanced for nanocrystalline materials compared to those that are microcrystalline. To prepare nanocrystalline materials there is a need for high-quality, nonagglomerated nanosized powders.

Several synthesis routes have been developed to produce nanocrystalline CeO_2-based powders, including precipitation with, e.g., hexamethylenetetramine,[6] ammonium carbonate,[7] and hydrazine;[8] solid-state reaction;[9] hydrothermal synthesis;[10−13] mechanochemical synthesis;[14,15] and combustion synthesis.[16−20] Powders prepared by a precipitation route usually consist of agglomerates,[12] which reduce the benefits of nanocrystalline powder when it comes to compacting and densification. Weakly agglomerated nanosized CeO_2 powders have been produced using a two-step precipitation process.[12,13]

CeO_2-based powders have been synthesized successfully by the combustion synthesis using different complexing agents/fuels such as glycine,[16,19,20] oxalyldihydrazide,[17] and carbohydrazide.[18] With the combustion synthesis a desired homogeneous high-purity powder can be produced in a short time at low cost and with

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simple equipment.[21] Due to the temperature increase during combustion, a low calcination temperature can be used. The large amount of gaseous products developed during the combustion limits particle contact and hence coarsening and agglomeration of the powder.

The aim of our work was to study the synthesis of high-quality nanocrystalline CeO_2-based powders (pure, CeO_2, gadolinium oxide and samarium oxide substituted CeO_2) by the glycine/nitrate combustion method. The influence of the G/N ratio on crystallite size, carbon-containing residues from the combustion, surface area, green density, shrinkage, and final density was examined. In addition, the influence of the calcination temperature on crystallite size and sintering properties were examined. Special emphasis was given to the presence of carbonate species in the powder, as caused by the combustion process.

Experimental Section

Synthesis. $Ce(NO_3)_3 \cdot 6H_2O$ (99.5%, Alfa Aesar), $Gd(NO_3)_3 \cdot 6H_2O$ (99.99%, Aldrich), or $Sm(NO_3)_3 \cdot 6H_2O$ (99.99%, Aldrich) were dissolved in deionized water to obtain a concentration of ~0.5 M of the cations. The individual precursor solutions were standardized thermogravimetrically by heating to 1000 °C to obtain the pure oxides. Solutions (~100 g) with correct stoichiometric amounts of the cations were mixed with glycine (Merck) to obtain G/N ratios of 0.30, 0.55, and 1.0, poured into an insulated tall beaker, and evaporated on a hotplate. For the substituted CeO_2 materials only a G/N ratio of 0.55 was used. After 2−3 h a highly viscous gel was formed and a fine mesh lid was placed on the top of the beaker to collect the powder during the following auto ignition. The different G/N ratios chosen correspond to fuel deficiency (0.30), near stoichiometric (0.55), and fuel excess (1.0) according to the definition by Chick et al.[21] A more violent reaction, where burning took place, was observed for the near stoichiometric and the fuel excess samples compared to the fuel deficiency sample.

The as-prepared powders were ball milled (yttria-stabilized zirconia media) for 12 h in ethanol, dried, and crushed in a mortar. The pure CeO_2 powders were further calcined at 400 °C for 20 h in a muffle furnace. To study the crystallite size of the pure CeO_2 powders as a function of calcination temperature, powders with G/N ratio = 0.55 were calcined at different temperatures. These powders were first calcined in a vertical tube furnace with oxygen flow (~5 mL/min) through the powder at 400 °C for 0.5 h followed by calcination in a muffle furnace at 500, 800, 900, or 1000 °C in air for 0.5 h. Some samples were only calcined in oxygen flow at 550 and 680 °C. The substituted CeO_2 powders were calcined in oxygen flow through the powders at 550 °C for ~12 h.

Characterization. The crystallite size of the as-prepared and calcined powders was calculated from X-ray diffractograms (XRD) (2θ range from 26° to 92°) acquired on a Siemens D5005 diffractometer. The computer programs PROFILE and WINCRYSIZE were used for the calculations. LaB_6 was used as a standard to determine instrument line broadening. The surface area of the as-prepared and calcined powders was measured by nitrogen adsorption (ASAP 2000, Micrometrics). Particle size was calculated from the surface area assuming spherical particles.

Infrared spectra of as-prepared and calcined powders were recorded in the 400−4000 cm^{-1} range (Bruker IFS 66v) by preparing KBr (Merck for spectroscopy) pellets (0.5 wt % sample). The microstructure of the pure CeO_2 powders was studied by transmission electron microscope (TEM) (Philips CM30). The powders were dispersed in acetone and deposited on a copper grid covered with carbon. Thermogravimetrical analysis, TGA, (Netzsch STA 449C) of as-prepared and calcined powders was performed in air by using a heating rate of 2 K/min up to 1000 °C.

Pellets (diameter 5 mm) of the calcined powders were uniaxially pressed. A pressure of ~300 MPa gave a green density of 55−57% of theoretical for calcined pure CeO_2 powders. For the calcined substituted CeO_2 powders a pressure of ~50 MPa gave a green density of 41−43% of theoretical. Higher pressures introduced pressing defects. Shrinkage of the green bodies up to 1450 °C was measured using a dilatometer (Netzsch DIL 402 C) with a heating rate of 2 K/min. The final density was measured by the Archimedes' method using 2-propanol. The crystallographic densities determined for coarse-grained heat-treated samples, 7.22, 7.24, and 7.15 g/cm^3 for pure CeO_2, $(GdO_{1.5})_{0.2}(CeO_2)_{0.8}$, and $(SmO_{1.5})_{0.2}(CeO_2)_{0.8}$, respectively, were used as theoretical densities.

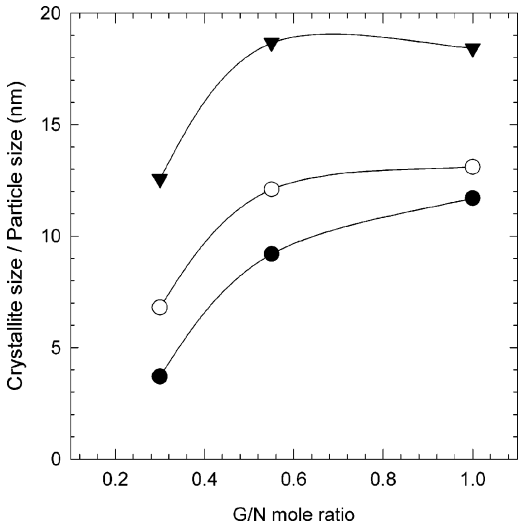

Figure 1. Crystallite size and particle size, calculated from BET surface area, for pure CeO_2 as a function of G/N ratio: ● = as-prepared powder, ○ = calcined at 400 °C for 20 h, and ▼ = BET particle size as-prepared powder. The lines are drawn as a guide to the eyes.

Results

Powder Characteristics. The influence of the G/N ratio on the crystallite size of the as-prepared pure CeO_2 powder and powder calcined at 400 °C is shown in Figure 1. Included in the figure is also the particle size of the as-prepared powder calculated from the surface area. The crystallite/particle size increases up to a G/N ratio of 0.55, whereas a further increase in G/N ratio did not cause any increase in the crystallite/particle size. The crystallite size of the calcined powders was slightly larger than that of the as-prepared powders. The surface area of the as-prepared powder with the G/N ratio of 0.3 was 66 m^2/g and the powders with G/N ratios 0.55 and 1.0 had a surface area of 45 m^2/g. The particle size calculated from the surface area was larger than the crystallite size calculated from the diffractograms. A TEM micrograph of the as-prepared pure CeO_2 powder with G/N ratio of 0.55 is shown in Figure 2. The size of the crystallites observed by TEM confirms the crystallite size obtained by XRD.

X-ray diffractograms of the as-prepared pure CeO_2 powders with different G/N ratios are shown in Figure 3. The diffraction lines are broader for the powder with lowest G/N ratio which corresponds with the smaller crystallite size. The observed color of the powders before calcination was light yellow for the fuel deficient ratio,

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Table 1. Lattice Parameter, Surface Area, Particle Size Calculated from Surface Area, and Crystallite Size of Pure CeO_2, and Sm_2O_3- and Gd_2O_3-Substituted CeO_2 after Calcination at 550 °C in Oxygen Flow

	pure CeO_2	$(GdO_{1.5})_{0.2}(CeO_2)_{0.8}$	$(SmO_{1.5})_{0.2}(CeO_2)_{0.8}$
lattice parameter [Å]	5.4104	5.4228	5.4331
surface area [m^2/g]	37	44	44
particle size [nm]	22	19	19
crystallite size [nm]	12.6	10.3	8.2

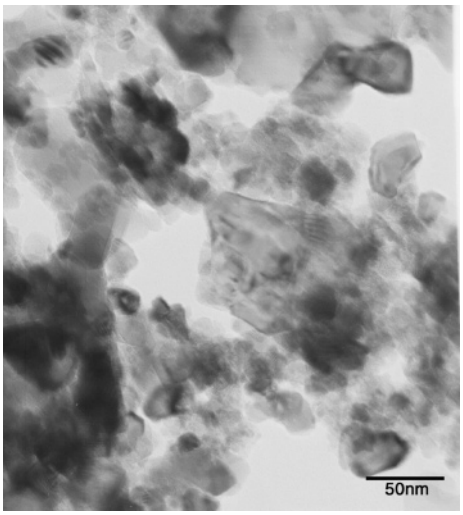

Figure 2. Transmission electron micrograph of as-prepared pure CeO_2 powder with G/N ratio of 0.55.

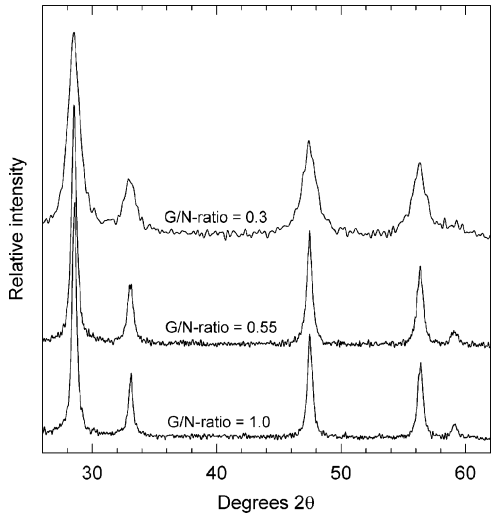

Figure 3. X-ray diffraction pattern of as-prepared pure CeO_2 powders with different G/N ratios.

off-white for the near stoichiometric ratio, and grayish for the fuel excess ratio. After calcination all the powders were pale yellow.

The combustion synthesis using the G/N ratio of 0.55 was studied further in more detail. The crystallite size and particle size of pure CeO_2 powders calculated from surface area are shown in Figure 4 as a function of calcination temperature. Crystallite growth initiates at a calcination temperature of ~700 °C.

The crystallite size of the calcined gadolinium oxide and samarium oxide substituted CeO_2 powders was measured to 10.3 and 8.2 nm and the surface area 43 and 44 m^2/g, respectively. Table 1 summarizes selected characteristics for the three CeO_2-based powders. The lattice parameters are in accordance with literature data.[22,23]

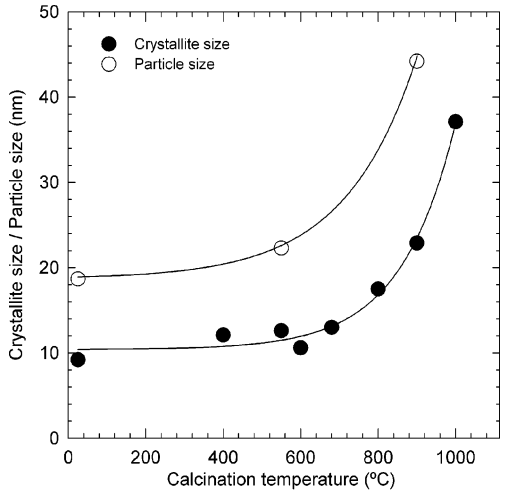

Figure 4. Crystallite size and particle size for pure CeO_2 as function of calcination temperature (G/N ratio of 0.55). The lines are drawn as a guide to the eyes.

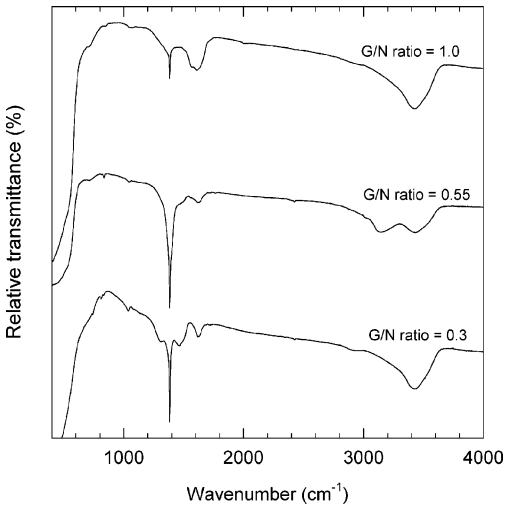

Figure 5. Infrared spectra of as-prepared pure CeO_2 powders with different G/N ratios.

FT-IR Spectroscopy. IR-spectra of the as-prepared pure CeO_2 powders produced with different G/N ratios are shown in Figure 5. The major features in the IR spectra are bands in the 1200−1700 and 3000−3800 cm^{-1} regions. In addition, the band due to the stretching frequency of Ce−O can be seen below 770 cm^{-1}. The bands in the frequency region from 1200 to 1700 cm^{-1} are assigned to carbonate species formed by coordination of CO_2 molecules onto the coordinatively unsaturated CeO_2 surface.[24] Bicarbonate-like species and monodentate carbonate species with O−C−O stretching frequen-

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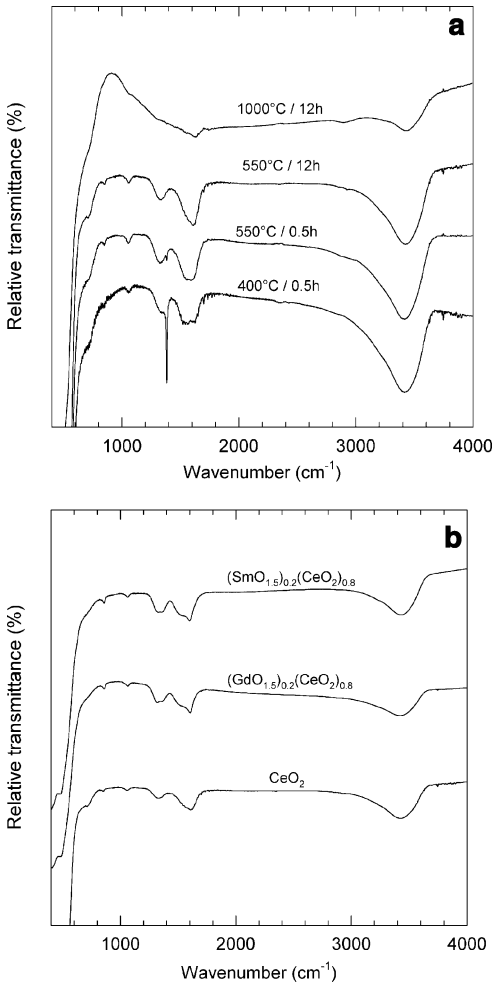

Figure 6. (a) Infrared spectra of pure CeO_2 powders calcined at different temperatures (G/N ratio of 0.55). (b) Infrared spectra of pure and substituted CeO_2 powders calcined at 550 °C (G/N ratio of 0.55).

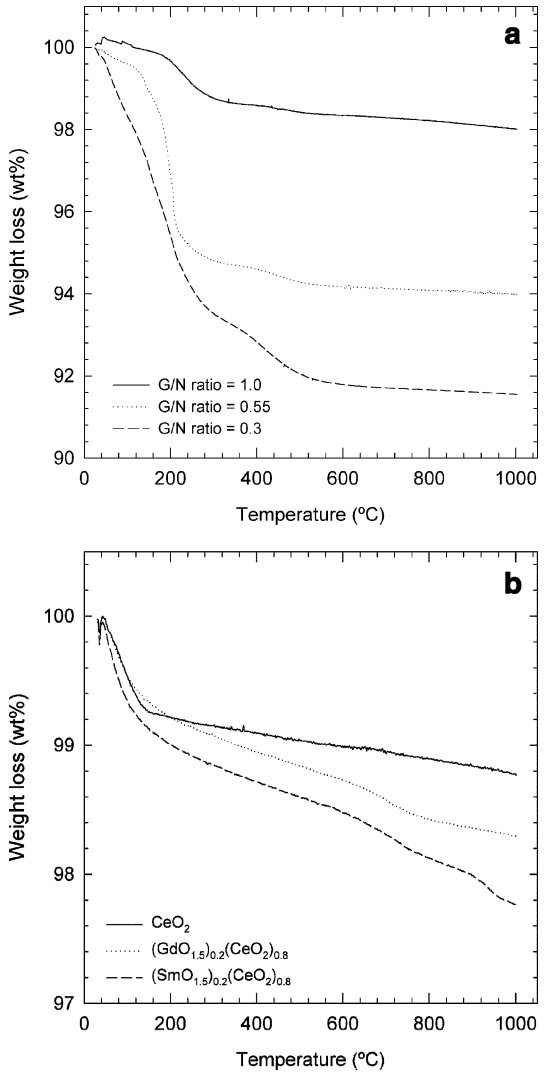

Figure 7. (a) Thermogravimetrical analysis of as-prepared pure CeO_2 powders with different G/N ratios. (b)Thermogravimetrical analysis of pure and substituted CeO_2 powders calcined at 550 °C (G/N ratio of 0.55).

cies of 1620 and 1430−1460 cm^{-1} are observed.[24] The 1620 cm^{-1} band is the most intense for high G/N ratio while the ∼1450 cm^{-1} feature is the most intense for the lower G/N ratios. The formation of bidentate carbonate species is observed for the low G/N ratio as a band at ∼1330 cm^{-1} is observed.[25,26] The strong band at 1383 cm^{-1} might be due to physically surface-adsorbed CO_2 due to the sharpness of the band. The intensity of this band decreases at the highest G/N ratio. The minor band located at 2410 cm^{-1} is due to linearly coordinated CO_2 adsorbed at the surface.[24] It cannot be excluded that the as-prepared powder with fuel deficiency contains some traces of nitrates giving contribution to the absorption at around 1400 cm^{-1}.[27]

The bands in the 3000−3800 cm^{-1} region can be attributed to O−H-stretching of physiosorbed H_2O or from surface Ce−OH groups. The "scissor" bending of H−O−H will have a broad absorption band located at about 1630 cm^{-1}.[24] This band is observed in the spectra and partly overlapping the O−C−O stretching band.

Selected IR-spectra as a function of the calcination temperature of the pure CeO_2 sample with G/N ratio of 0.55 are given in Figure 6a. The sharp band at 1383 cm^{-1} disappears during calcination (traces left after 0.5 h at 550 °C). The intensity of the peaks in the region 1200−1700 cm^{-1} due to carbonate-like species are decreasing significantly with increasing calcination temperature showing that the purity of the powder is increasing, however small amounts of carbonate species are left even after calcination at 1000 °C for 12 h.

The IR spectra for pure CeO_2, and gadolinium oxide and samarium oxide substituted CeO_2 calcined in oxygen flow at 550 °C for 12 h are compared in Figure 6b. There are no significant differences in the three powders considering the amount of carbonate-like species.

Thermogravimetric Analysis. Thermogravimetric data for the as-prepared pure CeO_2 powders with the three different G/N ratios are shown in Figure 7a. The observed weight loss decreases with increasing G/N ratio. The total weight loss up to 1000 °C is about 8.5%, 6.0%, and 2.0% for the G/N ratios of 0.3, 0.5, and 1.0, respectively. The figure shows two thermal events at 150−200 °C and above 400 °C. The first event is due to

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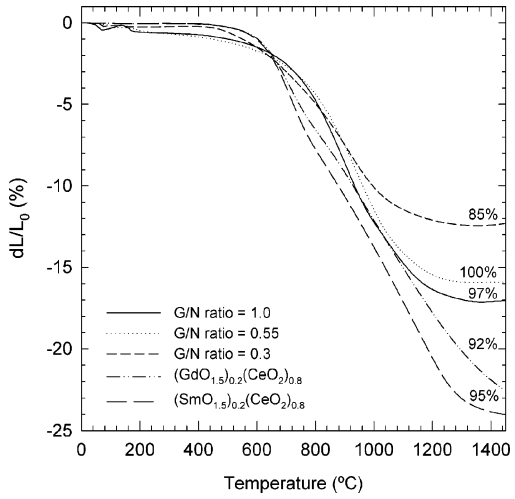

Figure 8. Linear shrinkage during sintering of pure CeO_2 calcined at 400 °C for 20 h with different G/N ratios, and Sm_2O_3- and Gd_2O_3-substituted CeO_2 calcined at 550 °C for 12 h with G/N ratio of 0.55.

the loss of adsorbed H_2O and CO_2 on the surface of the powder, whereas the second event is caused by the decomposition of carbonates.

Thermogravimetric analysis of the calcined pure CeO_2 and the substituted powders is given in Figure 7b. Prior to the measurement, the samples were heat-treated in air at 550 °C. The data show that the high-surface-area powders adsorb water and/or CO_2 which is relieved at about 100 °C. In addition a steady weight loss is observed up to 1000 °C showing the decomposition of carbonate species.

Densification Behavior. Linear shrinkage during heating is shown for powder compacts of calcined (400 °C/20 h) pure CeO_2 with different G/N ratios and calcined (550 °C/12 h) substituted CeO_2 powders in Figure 8. The difference in absolute total shrinkage is due to differences in green densities and achieved final densities. The pure CeO_2 sample made with fuel deficiency had an early on-set of sintering but did not achieve high density, whereas the pure CeO_2 powders with two highest G/N ratios showed similar sintering behavior. The onset of sintering for the substituted CeO_2 materials were somewhat lower than that for the pure CeO_2 (near stoichiometric and fuel excess).

Discussion

The function of glycine during the synthesis is 2-fold: first, it acts as a complexing agent for the cations in the nitrate solution; second, it is the fuel during the following combustion. Glycine has two functional groups and can in theory complex two moles of cations per mole. Hence, to ensure homogeneous mixing if several cations are present, a glycine to cation (G/C) ratio above 0.5 should be chosen. Here, the G/N ratios used correspond to G/C ratios of 0.90, 1.65, and 3.0, hence all the samples have excess glycine relative to complete complexation by glycine. To control the combustion reaction, the fuel (glycine) to oxidizer (nitrate) ratio can be varied and a stoichiometric G/N ratio, as defined by Chick et al.,[21] requires that no atmospheric oxygen is consumed during the combustion. In addition, only H_2O, CO_2, and N_2 are produced as gaseous species during the combustion. Equation 1 therefore describes a stoichiometric reaction for the present system.

$$9\ Ce(NO_3)_3{\cdot}6H_2O + 14\ NH_2CH_2COOH \rightarrow 9\ CeO_2\ (s) + 4^1/_2\ N_2\ (g) + 28\ CO_2\ (g) + 89\ H_2O\ (g) \quad (1)$$

Equation 1 corresponds to a G/N ratio of 0.52, hence our chosen ratio of 0.55 is close to a stoichiometric reaction as defined by Chick et al.[21] During the combustion synthesis a red brownish colored gas was observed which shows the formation of nitrous gases during the combustion. The real reaction taking place is therefore somewhat different from reaction 1.

The adiabatic flame temperature, assuming solid reactants, for the stoichiometric ratio, eq 1, was calculated to 1220 °C using data from Perry et al.[28] and Lide et al.[29] The adiabatic flame temperature is increasing with increasing G/N ratio. Chick et al.[21] have observed an increase in the measured flame temperature for the combustion of glycine-nitrate chromite precursors prepared at various glycine/nitrate ratios ($T \approx 1160$ °C at G/N = 0.4 and $T \approx 1450$ °C at G/N = 0.55). Above this G/N ratio a decrease in the measured flame temperature was recorded. Our observation of a more violent combustion for near stoichiometric and fuel excess samples can be explained by a higher real flame temperature for these reactions compared to that of the fuel deficient sample.

The increase in crystallite/particle size of pure CeO_2 (Figure 1) and the decreased broadening of the XRD pattern (Figure 3) are consistent with an increase in real flame temperature with increasing G/N ratio. An increase in crystallite size (G/N = 0.3, 100%; G/N = 0.55, 30%; G/N = 1.0, 10%) was measured after calcination at 400 °C for 20 h (Figure 1). The difference in crystallite growth during the calcination at 400 °C confirms an increasing real flame temperature with increasing G/N ratio. The significant increase in crystallite size after calcination at 400 °C indicates that the real flame temperature during the combustion was significantly below the adiabatic flame temperature.

A larger particle size calculated from the surface area than the crystallite size measured by XRD illustrates that the powder is to some extent agglomerated (Figure 1). Partial agglomeration is confirmed in the TEM micrograph of the as-prepared pure CeO_2 powder with G/N ratio of 0.55 (Figure 2). Less agglomeration is observed for the pure CeO_2 powder produced by using G/N ratio of 1.0 as the relative difference between the crystallite size and particle size is smaller than for the other two ratios (Figure 1). The generation of more gaseous products with increasing fuel content is expected to be beneficial to reduce agglomeration of the powder.

The purity of the powder can be evaluated from the IR spectra and the TG data. CeO_2 powder easily forms carbonate species on the surface as was observed from the IR spectra in Figures 5 and 6. With increasing G/N ratio, the intensity of the bands at around 1430−60

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cm^{-1} is weakened relative to the band at 1620 cm^{-1}. Such a change is also occurring with increasing calcination temperature (Figure 6a). Hence, the observed change in intensity is in accordance with the higher real flame temperature with increasing G/N ratio. Significant amounts of carbonate species are present up to about 800 °C, and even after calcination at 1000 °C for 12 h traces of carbonate species are left. The amount of surface-adsorbed CO_2 and H_2O released at 150−200 °C during heat treatment (Figure 7a) of the samples is increasing with decreasing real flame temperature. In addition, a larger weight loss due to removal of organic residues or carbonate species occurring at around 400 °C is observed in the fuel deficient sample (G/N ratio = 0.3) compared to the two other samples (Figure 7a). The relatively large weight loss of the sample with G/N ratio of 0.3 shows that the real flame temperature during reaction was low. The powder with G/N ratio of 0.3 might be due to the low real flame temperature containing traces of nitrates which will contribute to the weight loss around 200 °C as this is the decomposition temperature of Ce-nitrate.[29] The TG data for the calcined powders (Figure 7b) show a small weight loss of the samples up to 1000 °C due to the loss of carbonate species. The larger weight loss for the substituted materials reflects the more basic nature of the 3 valent substituted cations. The presence of carbonates was for the pure CeO_2 observed in the IR spectra (Figure 6a) up to 1000 °C in agreement with the TG data.

The pure CeO_2 powder compact prepared with fuel deficiency showed an onset of sintering at a lower temperature than the two other pure CeO_2 powders due to the smaller particle size. However, the overall sintering properties were not as good as the two powders prepared with near stoichiometric or fuel excess G/N ratios. The higher final density using the powders with G/N ratios of 0.55 and 1.0 shows the necessity of producing a powder with a high degree of purity, i.e., free from C containing residues from incomplete combustion. The earlier onset of sintering for the samarium oxide and gadolinium oxide substituted samples compared to pure CeO_2 (near stoichiometric and fuel excess) is due to significantly increased oxygen vacancy concentrations.[30]

Conclusion

Nanocrystalline CeO_2, $(GdO_{1.5})_{0.2}(CeO_2)_{0.8}$, and $(SmO_{1.5})_{0.2}(CeO_2)_{0.8}$ powders were successfully synthesized using combustion synthesis with glycine as the fuel and nitrate as the oxidizer. The optimal route for synthesis of nanocrystalline CeO_2-based powders involves the use of a G/N ratio around 0.55 and calcination at 550 °C in oxygen flow. A high-quality, highly reactive powder with a crystallite size of about 10 nm was prepared using this route. Onset of sintering was at about 600 °C for CeO_2 and high density was obtained at ∼1300 °C.

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