Hydrothermal synthesis and characterization of rare earth doped ceria nanoparticles


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Abstract

Ceria (CeO\textsubscript{2}) and rare earth doped ceria (RE = Pr, Gd and Sm) of different doping concentration (10, 20 and 30 mol\%) were synthesized by hydrothermal synthesis method, achieving nano-particles with weak agglomeration. The nano-particles were studied using X-ray diffraction (XRD), transmission electron microscopy (TEM), BET specific surface area measurement and thermal analysis. The size of all doped nano-particles was in the range of 13–25 nm, while the un-doped ceria nano-particles were in the range of 12–16 nm. The effect of precursor concentration on microstructure and morphology of the final powder is reported in this paper. The increase of precursor concentration led to decreases in crystallite size, increase in lattice parameter and increase in the BET specific surface area with Ce\textsuperscript{3+} from 0.005 to 0.015 M. The highest rare earth doping ratio is found to be 20, 10 and 20 mol\% for Pr, Gd and Sm, respectively.

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Keywords: Hydrothermal; Ceria; Nano-particles; Rare earth

1. Introduction

Ceria (CeO\textsubscript{2}) is widely used in solid oxide fuel cells (SOFC), catalysis, polishing agents and luminous materials [1,2]. Rare earth doped ceria is considered one of the most promising electrolyte materials for SOFC [3]. These materials possess high ionic-electronic conductivity at relatively low temperatures. The synthesis of nano-sized ceria and rare earth doped ceria has been extensively studied. Common synthesis approaches include hydrothermal and solvothermal synthesis [4–7], sol–gel synthesis [8–10], spray pyrolysis [11]. The hydrothermal process has attracted a lot of attention because nanoparticles of desired size and shape can be easily produced due to ease to control of processing parameters like solution pH, reaction temperature, reaction time, solute concentration and the type of solvent [12]. The homogeneous nucleation in hydrothermal synthesis makes it possible to achieve nano-particles with very small grains and high purity [13].

There is sufficient literature reporting on the effects of hydrothermal processing parameters on the particle structure and morphology. However, there is lack of information on the effect of different rare earth dopants on the structure and morphology in comparison with un-doped ceria. This paper report on the synthesis of ceria and rare earth doped ceria (RE = Pr, Gd and Sm) by hydrothermal processing and how the precursor concentration affects the different rare earth doped ceria nano-particles.

2. Experimental procedures

Un-doped and doped (RE = Pr, Gd and Sm) ceria nano-particles were synthesized by hydrothermal method. Precursors used were cerium carbonate (Ce\textsubscript{2}O\textsubscript{3}/TREO 60.5%), praseodymium(III) carbonate (Pr\textsubscript{2}(CO\textsubscript{3})\textsubscript{3}·3H\textsubscript{2}O) 99.99%, gadolinium(III) carbonate (Gd\textsubscript{2}(CO\textsubscript{3})\textsubscript{3}·3H\textsubscript{2}O) 99.9%, samarium(III) carbonate (Sm\textsubscript{2}(CO\textsubscript{3})\textsubscript{3}·3H\textsubscript{2}O) and hexamethylenetetramine (HMT) (C\textsubscript{6}H\textsubscript{12}N\textsubscript{4}, ≥99.5%). Cerium(III) nitrate hexahydrate (CeN) solution was achieved by reacting cerium carbonate with nitric acid and diluted to varying concentrations (0.005, 0.01, 0.015, 0.02 and 0.025 M). Hexamethylenetetramine (HMT), which served as a precipitating agent was added to cerium(III) nitrate drop-wise in the molar ratio of 5:1 (HMT:CeN) under continuous stirring. The pH of the CeN–HMT solutions was maintained at near neutral condition. The CeN–HMT aqueous solutions were hydrothermally treated...
in tightly capped Pyrex test bottles at 100 °C for 2 h, and were cooled in the hydrothermal oven overnight. The ceria powder was obtained by centrifuging and washing with deionized water, followed by oven drying.

The rare earth carbonates (RE₂(CO₃)₃·3H₂O, RE = Pr, Gd and Sm) were added slowly into stirred nitric acid over a slight heat of 60–70 °C until a clear solution was achieved to produce rare earth(III) nitrate hexahydrates. Rare earth doped ceria nanoparticles were prepared by hydrothermal treatment at 100 °C for 2 h with 400 ml aqueous solutions containing variable concentrations (10, 20, 30 mol%) of rare earth nitrate and cerium nitrate (0.01 M) in the presence of HMT (0.05 M) as the precipitating agent. The solutions were hydrothermally precipitated in tightly capped Pyrex bottles and the obtained precipitates were centrifuged, washed and dried.

Un-doped single phase cerium oxide (CeO₂) was prepared via hydrothermal precipitation of the cerium(III) nitrate hexahydrate (Ce(NO₃)₃·6H₂O) with hexamethylenetetramine (HMT) under the selected conditions (100 °C, pH 7, 2 h). In the course of the hydrothermal process, there was a color change from white (cerium(III) hydroxide) to violet (cerium(IV) hydroxide). The presence of pale yellowish color precipitates after hydrothermal treatment, washing and drying was strong evidence of the ceria formation.

X-ray diffraction (XRD, Shimadzu 6000) was used for phase identification, crystal size and lattice parameter calculation. Thermal analysis was performed by differential thermal analysis (DTA, Netzsch STA 449C) at the heating rate of 10 °C/min. BET specific surface area was measured using a Micrometrics ASAP 2000 with nitrogen at about 77 K. Powder morphology and size were studied by transmission electron microscopy (TEM, JEOL JEM 2010).

3. Results and discussion

3.1. Un-doped ceria

The TG/DTA results of the thermal decomposition process for cerium oxide (0.01 M) is shown in Fig. 1. The weight loss indicates the decomposition of hydrated oxide, i.e. CeO₂·H₂O to CeO₂. This amount of weight loss was low, which suggests that the samples consisted of a mixture of more CeO₂ than the hydrated ceria, also attributed to the low hygroscopic nature of CeN [14,15]. Three major weight losses are seen. The poorly resolved first step (I) accounted for 1.74 mg weight loss up to 102.4 °C due to dehydration of the hydrated CeO₂, which produced an endothermic peak. The second (II) weight loss was about 1.26 mg, and an exothermic peak is seen at 236.5 °C. This exothermic peak corresponded to the crystallization of CeO₂ and the oxidation of Ce³⁺ [16]. Further increase in temperature beyond 200 °C also triggered the decomposition of the anhydrous salt, contributing to the second weight loss. The third (III) step accounts for weight loss due to the decomposition of residual nitrate. The overall weight loss was not entirely due to dehydration alone.

Fig. 2 shows the XRD patterns for un-doped cerium oxide synthesized from different CeN concentrations (0.005, 0.01, 0.015, 0.02 and 0.025 M). The XRD diffraction patterns indicated that all the synthesized nano-powder was cerium oxide (JCPDS card: 34-0394). The crystallite sizes and the lattice parameters were calculated from the XRD peak broadening and shifting. Fig. 3 shows the crystallite size of the synthesized powder as a function of the Ce³⁺ concentration. The crystallite sizes of the ceria nano-powders ranged from 12 to 16 nm and were found to decrease with the increase of the Ce³⁺ concentration. As the (Ce³⁺:HMT) ratio was fixed at 1:5, the high Ce³⁺ concentration sample will have higher HMT content and hence more alkaline than low Ce³⁺ concentration solution. It was also reported by Wu et al. [17] that the crystallization of the nanoparticles synthesized in an acidic hydrothermal medium was more complete than others, thus it is likely that the decrease in crystallite size with the increase in Ce³⁺ concentration is due to the increase in HMT content. With more HMT in the precursor solution, the time for the nano-crystal growth was reduced, resulting in less crystallinity and finer particles [18]. For doping purposes, the ceria prepared by 0.01 M Ce precursor concentration was selected to dope with other rare earths.

![Fig. 1. TG/DTA curve of 0.01 M CeO₂.](image)

![Fig. 2. XRD peaks for un-doped cerium oxide at 0.005, 0.01, 0.015, 0.02 and 0.025 M.](image)
Fig. 3. Plot of crystallite size vs. Ce$^{3+}$ concentration.

Fig. 4 plots the lattice parameter of un-doped ceria as a function of Ce$^{3+}$ concentration. The lattice parameter increased with the increase in Ce$^{3+}$ concentration. The lattice expansion of ceria nano-particles was due to the decrease in crystallite size with the increase of Ce$^{3+}$ concentration. Such relationship can be accounted for via various reasons: lattice stress/strain condition or the effects of Ce$^{3+}$ oxidation to Ce$^{4+}$ process. Zou et al. [19] suggested that the variation in the lattice parameter occurs due to the surface stress on ceria crystals. This stress transpires due to hydrogen bonding between adsorbed atoms in the solution with oxygen atoms within the lattice. Ce$^{3+}$ ions have a higher ionic radius (1.034 Å) as compared to the Ce$^{4+}$ ions (0.92 Å). Introduction of oxygen vacancies and accompanying Ce$^{3+}$ ions led higher distorting of the local symmetry. This often causes the change in the Ce–O bond length and the overall lattice parameter, $a$.

Under the current synthesis method, it was necessary for the initial precursor to contain only Ce$^{3+}$ and oxidized to Ce$^{4+}$ during the hydrothermal treatment process to achieve finer particles. The solution containing the higher amount of cerium(III) will require a long time for conversion of Ce$^{3+}$ into Ce$^{4+}$ [20]. Zhou and Huebner [21] studied the influence of particle size on the Ce$^{3+}$/Ce$^{4+}$ ratio in CeO$_2$ nano-particles. In their work, a higher concentration of Ce$^{3+}$ was present in the finer particle sizes. The expansion of the lattice with decreasing particle size observed in this report also compliments Tsunekawa et al.’s work [22].

Another interesting observation is the peak shift with crystal size. In the case of a finer crystal, the peak shifted to smaller 2$\theta$ angles, corresponding to a larger $d$-spacing. The use of high pressure of O$_2$ in the reacting bottles for hydrothermal treatments was reported to contribute for a better stoichiometric ceria [23].

Fig. 5 shows the crystallite size and the BET specific surface area ($S_{BET}$) corresponding to the cerium concentration. The $S_{BET}$ of the nano-ceria increased from 0.005 M cerium oxide sample to a maximum point at 0.015 M cerium oxide sample, and subsequently followed by a sharp decline in $S_{BET}$ for 0.02 and 0.025 M ceria samples. Theoretically, the BET specific surface area should increase with the decrease in crystallite size. However, Fig. 5 shows a sudden decrease in surface area of the smaller crystallite sized ceria. This can be accounted for by the effect of agglomeration. The agglomeration of the fine nano-particles was also observed in the TEM images described later.

Fig. 6 shows the TEM micrographs and electron diffraction pattern of the synthesized ceria using different concentration. The particle size was measured from the TEM micrographs and compared with XRD calculations. Table 1 lists the comparison of particle size measured by TEM and crystallite size calculated from XRD. These two results match well on the samples using low Ce concentration, but there was a larger difference when

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<table>
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<th>Ce concentration (M)</th>
<th>Average XRD crystallite size (nm)</th>
<th>Average TEM particle size (nm)</th>
</tr>
</thead>
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<tr>
<td>0.005</td>
<td>16</td>
<td>20</td>
</tr>
<tr>
<td>0.01</td>
<td>14</td>
<td>15</td>
</tr>
<tr>
<td>0.015</td>
<td>13</td>
<td>11</td>
</tr>
<tr>
<td>0.02</td>
<td>12</td>
<td>21</td>
</tr>
<tr>
<td>0.025</td>
<td>12</td>
<td>25</td>
</tr>
</tbody>
</table>
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Fig. 6. TEM micrograph of synthesized CeO₂ at the concentration of: (a) 0.005 M, (b) 0.01 M, (c) 0.015 M, (d) 0.02 M, (e) 0.025 M and (f) diffraction pattern (0.01 M sample).
compared with the samples synthesized using Ce concentration (0.02 and 0.025 M). All primary crystallites were agglomerated into uniform agglomerates. The agglomerate size distribution was in the range of 1–8 μm. Agglomeration usually increases with the decrease in particle size due to higher surface energy. There was no clear trend of agglomerate size with the Ce concentration due to the wide distribution of agglomerate size.

3.2. RE-doped (RE = Pr, Gd and Sm) ceria

Figs. 7–9 show the XRD pattern of Pr, Gd and Sm-doped ceria samples at varying concentration. This variation was performed to study the effects of rare earth doping concentration on the composition and morphological characteristics of the nano-powders.

Pr-doped ceria was characterized a brick red color powder. For the 10 and 20 mol% Pr-doped samples, the XRD results display nearly all of the characteristics reflections corresponding to the fluorite structure of CeO₂ (JCPDS card no. 34-0394). But for the 30 mol% Pr-doping sample, the XRD results display addition peaks of Ce(OH)₃, which did not oxidize to cerium oxide during the process [24]. It should be noted that under current synthesis conditions, the highest Pr amount that could be incorporated into the uniform particles should be lower than 20 mol%, and this also agrees well with the conclusions of Rojas and Ocana [25]. Pale yellow Gd-doped ceria was achieved [23]. XRD analysis indicates that the as prepared Gd-doped nano-powders have a cubic fluorite structure. Un-reacted Ce(OH)₃ precursor was observed in Gd/Ce samples 20 and 30 mol% [24]. Phase identification was done on the three different doped samples and it was suggested that the maximum Sm-doping was limited to 20 mol% Sm under the stated hydrothermal process conditions. The hydrothermal synthesis was not successful for 30 mol% Sm-doped samples. The other Sm-doped samples were identified to have the fluorite structure of CeO₂ (JCPDS: 34-394) [26]. Lanthanides readily form carbonate or hydroxyl carbonate solid solutions among each other, due to their similar chemical properties [27].

The crystallite size was calculated using the Scherrer equation for un-doped and RE-doped ceria. Table 2 lists the comparison of crystallite size. The crystallite size of RE-doped ceria is found to decrease with the increase in doping concentration. In many situations, subsequent nucleation of each rare earth components requires different pH, temperature or need a longer synthesis time [28]. As the rare earth content increased for the doping, the

<table>
<thead>
<tr>
<th>Doping content (mol.%)</th>
<th>Un-doped ceria (nm)</th>
<th>Pr-doped ceria (nm)</th>
<th>Gd-doped ceria (nm)</th>
<th>Sm-doped ceria (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>14.01</td>
<td>16.11</td>
<td>16.5</td>
<td>13.89</td>
</tr>
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<td>20</td>
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<td>14.5</td>
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</tr>
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<td>30</td>
<td>14.01</td>
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</table>
crystallization of the precursors was hindered leading to smaller crystallite sizes.

Peak shift in XRD results was observed in the RE-doped ceria. Lattice constant was calculated on the basis of peak shifting. Table 3 gives the lattice constant comparison between the un-doped and RE-doped ceria samples. The slight shift of XRD peaks to lower \(2\theta\) values for the Pr-doped ceria suggests the formation of Pr–CeO\(_2\) solid solution. The lattice constant for un-doped ceria reported a value of 5.42 Å.

Pr\(^{3+}\), Gd\(^{3+}\), Sm\(^{3+}\) have an ionic radius of 0.1126, 0.1053 and 0.108 nm, respectively [26]. As the rare earth cations have larger ionic radius than Ce\(^{4+}\) (0.097 nm), the lattice constant increases with the increase in doping concentration observed. The substitution of the Ce\(^{4+}\) sites with larger rare earth cations will increase the lattice parameter.

The morphology of rare earth doped ceria was observed by TEM. Figs. 10–12 show the nano-particles morphology for the Pr, Gd and Sm doped ceria, respectively. Spherical shaped particles with uniform size distribution were observed. The average size of the nano-particles for doped ceria agrees with the calculation from XRD results, slight agglomeration was observed.

Table 4 displays the comparison of BET specific surface areas of the un-doped and RE-doped (RE = Pr, Gd and Sm) ceria. The BET specific surface areas of Pr-doped ceria were higher than the un-doped samples (0.01 M ceria) and the values agree well with Rojas and Ocana (73.5 m\(^2\)/g) [25]. The BET value of 30 mol% Pr-doped sample was higher than the other two sample with lower doping concentration, which may due to the presence of small amount of Ce(OH)\(_3\), as confirmed by the XRD results. The values for 10 and 20 mol% Gd-doped ceria BET values

<table>
<thead>
<tr>
<th>Doping content (mol.%)</th>
<th>Un-doped ceria (m(^2)/g)</th>
<th>Pr-doped ceria (m(^2)/g)</th>
<th>Gd-doped ceria (m(^2)/g)</th>
<th>Sm-doped ceria (m(^2)/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>60.27</td>
<td>72.57</td>
<td>43.71</td>
<td>52.87</td>
</tr>
<tr>
<td>20</td>
<td>60.27</td>
<td>70.60</td>
<td>44.85</td>
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</tr>
<tr>
<td>30</td>
<td>60.27</td>
<td>80.51</td>
<td>76.63</td>
<td>19.67</td>
</tr>
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</table>

Rojas and Ocana (73.5 m\(^2\)/g) [25]. The BET value of 30 mol% Pr-doped sample was higher than the other two sample with lower doping concentration, which may due to the presence of small amount of Ce(OH)\(_3\), as confirmed by the XRD results. The values for 10 and 20 mol% Gd-doped ceria BET values.
agree with the literature of 44.4 m²/g [29]. A higher BET specific surface area value was observed for 30 mol% Gd-doped sample, which indicates the smaller crystallite size. The unreacted precursor may cause the high BET specific surface area value as well. With an increase in the dopant concentration, BET specific surface area of Sm-doped ceria increased. However, for the 30 mol% Sm-doped ceria a very low value was measured, which was not conclusive.

4. Conclusion

Un-doped and RE-doped ceria (RE = Pr, Gd and Sm) nanoparticles were achieved by hydrothermal processing method. The powders were studied by XRD, TEM, BET specific surface area and thermal analysis. The un-doped ceria nano-particles had a size range of 12–16 nm, and the crystallite size decrease with the increase of Ce³⁺ concentration. The lattice parameter increased with the increase in Ce³⁺ concentration. The BET specific surface area of the un-doped ceria increased with the increase in Ce³⁺ from 0.005 to 0.015 M, and decreased significantly with the 0.02 and 0.025 M samples. The TEM particle size results of the un-doped sample agree with the XRD results and slight agglomeration is observed. Under the current synthesis condition, RE-doped ceria samples having size range of 12–16 nm, and the highest rare earth doping ratio was found to be 20, 10 and 20 mol% for Pr, Gd and Sm, respectively. The crystallite size of RE-doped ceria was found to decrease with the increase in RE content. The lattice parameter was found to slightly increase with the increase in RE-doping content. The BET specific surface area was found to increase with the increase in RE-doping content, due to the decrease in particle size.

References
