

Mechanical stirring and synergistic effect of $\text{Pr}^{3+}/\text{Pr}^{4+}$ and Ce^{4+} in improving the low-temperature reducibility of Pr-doped ceria nanoparticles

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Abstract — We report that shape/size-controlled high surface area CeO_2 and Pr-doped CeO_2 solid solution nanoparticles were synthesized using a facile hydrothermal method. The effect of mechanical stirring during the initial stage of synthesis on the shape/size control, phase homogeneity of mixed oxides, and reducibility of materials were investigated. The results indicate that a synergistic effect between Ce^{4+} and $\text{Pr}^{3+}/\text{Pr}^{4+}$ in the Pr-doped CeO_2 nanoparticles facilitates oxygen mobility within the solid solution lattice structure hence improving the reducibility of doped ceria materials at lower temperature as compared to the pure CeO_2 . Characterization techniques that were employed in this study include Powder X-ray diffraction (XRD), Transmission Electron Microscopy (TEM), BET surface area and Hydrogen Temperature Programmed Reduction (H_2 -TPR).

Keywords— Hydrothermal synthesis, rare-earth oxides, shape/size control, reducibility.

I. INTRODUCTION

Ceria (CeO_2) based materials are considered important in the chemical industry due to their applications in optical films, polishing materials, gas sensors, fuel cells and more importantly in the field of catalysis. Ceria is one of the extensively used catalysts in the three way catalytic converters where combustion engine exhaust gases, such as CO , NO , H_xC_y , are efficiently converted to environmentally friendly gases [1] – [5].

Pure Ceria suffers from low thermal stability at high temperatures (e.g. $>800^\circ\text{C}$). Doping of CeO_2 with various metal oxides, e.g. praseodymium or zirconium or titanium-based oxides, to generate metal oxide solid solutions can boost its thermal stability and its low-temperature redox functionality or oxygen capacity [6], [7]. For example, nano-sized cerium based mixed oxides, such as $\text{Ce}_{1-x}\text{Pr}_x\text{O}_2$, $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$, and $\text{Ce}_{1-x}\text{Ti}_x\text{O}_2$ have higher catalytic performance as compared to pure cerium oxide nanoparticles; their high catalytic performance is in general agreeably attributed to their

enhanced thermal stability and easier formation of oxygen vacancies in the CeO_2 cubic fluorite structure, hence leading to a higher oxygen ion mobility within the lattice structure [8], - [9].

The goal of this present work is to investigate the effects of stirring on the formation of solid solutions of Pr-doped CeO_2 , and on the shape/size control of the synthesized nanoparticles, and the Pr doping effect in CeO_2 on the low-temperature activity of materials.

II. EXPERIMENTAL

A. Sample Preparation

Pure CeO_2 and Pr-doped CeO_2 powders were prepared by hydrothermal method. To study the effect of mechanical stirring on the shape/size control of CeO_2 and on the phase homogeneity of Pr-doped CeO_2 during the initial stage of synthesis, one reactant mixture of pure CeO_2 and one consisting of Pr-doped CeO_2 were stirred for 20 minutes and 40 minutes, respectively, before loading them into sealed 100 ml Teflon lined autoclaves, while other two reaction mixtures each consisting of pure CeO_2 and Pr-doped CeO_2 were loaded into the autoclaves without stirring. In this paper, all the samples were hydrothermally treated at 150°C for 48 hours. In a typical procedure, 0.1 M $\text{Ce}(\text{NO}_3)_3$ and 0.1 M $\text{Pr}(\text{NO}_3)_3$ solutions were prepared by dissolving 8.68 g of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 8.70 g of $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, respectively, into 200 ml distilled water, while 6 M NaOH was prepared by dissolving 48 g of NaOH into 200ml of distilled water. As far as pure CeO_2 is concerned, two reaction mixtures containing 55 ml of 0.1M $\text{Ce}(\text{NO}_3)_3$ and 5 ml of 6M NaOH were prepared, after which one reaction mixture was loaded directly into the autoclave without stirring, while the other one was stirred vigorously for 20 minutes before loading it into the autoclave. On the other hand, two samples of $\text{Pr}_{0.3}\text{Ce}_{0.7}\text{O}_2$ nanopowders were synthesized in the same manner as described above except that for each reaction setup, 38.5ml of 0.1 M $\text{Ce}(\text{NO}_3)_3$ and 16.5 ml of 0.1 M $\text{Pr}(\text{NO}_3)_3$ solutions were thoroughly mixed together first before 5 ml of 6 M NaOH were added to the mixtures. One of the Pr-doped CeO_2 reaction mixtures was stirred vigorously for 40 minutes while

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the other one was not stirred. The mixtures were then poured into sealed 100 ml Teflon lined autoclaves and hydrothermally treated at 150 °C for 48 hrs. The vessels were then cooled to room temperature. Final precipitates were then filtered and thoroughly washed with 500 ml of distilled water and 200 ml of ethanol, then dried at 40 °C for 12 hours.

B. Characterization

Powder X-ray diffraction (XRD) analysis was done using the Rigaku Miniflex II Desktop X-ray Diffractometer applying a scanning range of 10 to 90°. Transmission electron microscopy (TEM) was performed using a JEOL 2100 that was operated at 200 kV. BET surface area analysis was performed on the dry nanopowders at -196 °C using liquid nitrogen. All the samples were pretreated for 1 hour at 110 °C using helium gas before surface area measurements were conducted. Hydrogen temperature programmed reduction (H₂-TPR) experiments were performed on the samples immediately after BET surface area analysis. Both H₂-TPR and BET surface area experiments were performed in a Micromeritics AutoChemTM II 2920.

III. RESULTS AND DISCUSSION

A. X-ray diffraction and TEM characterization

Figure 1 presents the powder XRD profiles for the four samples (a: CeO₂-no stirring; b: CeO₂-20 min stirring; c: Ce_{0.7}Pr_{0.3}O₂-no stirring; d: Ce_{0.7}Pr_{0.3}O₂-40 min stirring) that were synthesized using hydrothermal method. All the reflections of the XRD patterns for three samples (a, b, d) can be indexed to the single phase of CeO₂ with a fluorite-like structure (JCPDS card 34-0394). No other phases were found in the Ce_{0.7}Pr_{0.3}O₂ sample (d), indicating the formation of oxide solid solution. However, for the Ce_{0.7}Pr_{0.3}O₂ sample that was prepared without mechanical stirring (sample c), the XRD pattern shows reflection peaks for Pr(OH)₃ (JCPDS card 045-0086) [9] and TEM image (Figure 2 c) also show the rod-like Pr(OH)₃ phase. This indicates that mechanical stirring is a critical prerequisite to the synthesis of compositionally homogenous oxide solid solutions using this method. It is also evident that the stirred samples (b: 3.9 nm and d: 3.2 nm) have a smaller particle size, compared to the unstirred samples (a: 9.8 nm and c: 11.1 nm), by analyzing XRD profiles using the Scherrer equation. A peak shift to lower reflection angles was observed for the Ce_{0.7}Pr_{0.3}O₂ sample (d), which is somewhat unexpected as Ce⁴⁺ (0.97 Å) and Pr⁴⁺ (0.96 Å) have similar ionic radii. The reason for this anomalous behavior is not yet clear at this moment, but it could be due to presence of some Pr³⁺ (1.126 Å) [1] – [5], [10].

Figure 1: Powder XRD profiles for four hydrothermally synthesized samples: (a) CeO₂ (no stirring); (b) CeO₂ (20 min stirring); (c) Ce_{0.7}Pr_{0.3}O₂ (no stirring); (d) Ce_{0.7}Pr_{0.3}O₂ (40 min stirring).

Figure 2 shows the corresponding TEM images for the four samples as described above. As it can be seen from Figure 2 (a), CeO₂ nanoparticles that were synthesized without stirring consists of well dispersed nanocubes that have a high symmetry and a high degree of *crystallinity*. On the other hand, Figure 2 (b) indicates that CeO₂ nanoparticles that were prepared by stirring presents irregular shape and a low degree of *crystallinity*, which is consistent with the XRD data with broader profiles for the unstirred samples as shown in Figure 1 (a) and (b). Figure 2 (c) represents the 30 wt.% Pr-doped ceria sample that was synthesized without stirring of the reactants. From the TEM image it is clear that the sample consisted of mixed morphology. The nanorods represent Pr(OH)₃ phase, which is responsible for the low BET surface area, as shown below. The mechanistic influence of stirring on particle size and morphology is not yet clear at this moment but one thing that comes out clearly is that growth habit of nanoparticles dictates their size and shape [11]. We are currently performing studies in order to understand how mechanical stirring of reactants affect the mechanism of crystal seed formation and growth.

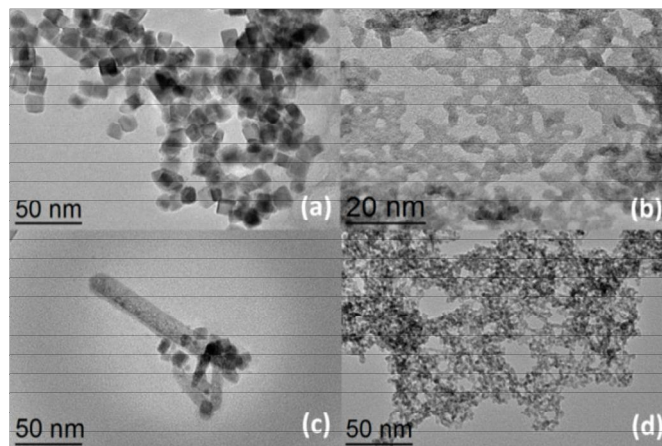


Figure 2: TEM images for four hydrothermally synthesized samples: (a) CeO₂ (no stirring); (b) CeO₂ (20 min stirring); (c) Ce_{0.7}Pr_{0.3}O₂ (no stirring); (d) Ce_{0.7}Pr_{0.3}O₂ (40 min stirring).

B. H₂-TPR and BET surface area analysis

Figure 3 presents the H₂-TPR profiles for the four samples as described above. As it is evident from the profiles, sample (a) shows better catalytic performance than the sample (b). Particularly, the sample (a) shows a higher H₂-consumption during surface reduction than during bulk reduction. This can be proved by the fact that the intensity for surface reduction peak on this particular profile is much higher than that of its bulk reduction. This phenomenon can be attributed to the dominantly exposed {100} crystallographic planes of nanocubes, which are believed to require less oxygen vacancy formation energies as compared to other crystallographic planes that may be dominantly exposed on particles of other morphologies e.g. the irregularly shaped morphologies that are represented on samples (b) and (d) [1] - [3].

The mixed oxides show on average much smaller particle sizes and have superior low-temperature reducibility, as shown in Figure 3. As it can be seen from Figure 3, pure CeO₂ samples show both surface and bulk reduction, while the Pr-doped CeO₂ samples are characterized only by surface reduction. As documented in literature [2], [3], this effect can be attributed to changes in the creation of vacancies in the lattice structure. By comparing Figure 3 (c) and (d), we can conclude that a uniform CeO₂/PrO₂ solid solution (sample d) shows lower surface reduction temperature and higher H₂ consumption, compared to the sample c which is characterized by a phase separation.

Figure 3: H₂-TPR profiles for four hydrothermally synthesized samples: (a) CeO₂ (no stirring); (b) CeO₂ (20 min stirring); (c) Ce_{0.7}Pr_{0.3}O₂ (no stirring); (d) Ce_{0.7}Pr_{0.3}O₂ (40 min stirring).

On running BET surface area analyses on the four samples, the samples (a), (b), (c) and (d) shows surface area of 84.0 m²/g, 111.0 m²/g, 42.3 m²/g and 136.07 m²/g, respectively. Table 1 below gives a summary of the particle size, BET surface area and reduction temperatures of the four

samples. These data are in good agreement with the TEM images shown above as far as their sizes and dispersion are concerned. For example, samples (b) and (d) show the highest specific surface areas, due to their small particle size and high dispersion while sample (a) shows a lower surface area due to a larger particle size though the particles are still well dispersed. Sample (c) shows the lowest surface area possibly due to the presence of larger size Pr(OH)₃ rod-like particles. As it can be noted from these results, doping of Pr on CeO₂ nanoparticles seems to significantly account for the increase on BET surface area and the improved low-temperature reducibility.

Table 1: A summary of the particle sizes, BET surface area and reduction temperatures for the synthesized samples.

Samples	Particle Size from XRD	BET surface area	Reduction Temperature
(a) CeO ₂ (no stirring)	9.8 nm	84.0 m ² /g	472 °C/759 °C
(b) CeO ₂ (20 min stirring)	3.9 nm	111.0 m ² /g	480 °C/788 °C
(c) Ce _{0.7} Pr _{0.3} O ₂ (no stirring)	11.1 nm	42.3 m ² /g	499 °C
(d) Ce _{0.7} Pr _{0.3} O ₂ (40 min stirring)	3.2 nm	136.1 m ² /g	483 °C

IV. CONCLUSIONS

We have shown that hydrothermal method can be used to synthesize Pr-doped CeO₂ mixed oxide nanopowders with superior low-temperature activity compared to pure CeO₂. The mechanical stirring plays a critical role in controlling shape/size of the synthesized CeO₂ and in forming compositionally homogeneous CeO₂-PrO₂ solid solution.

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