One-step synthesis of samarium-doped ceria and its CO catalysis

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Abstract. The samarium-doped ceria (SDC) nanospheres were prepared by the one-step hydrothermal method and characterized by transmission electron microscope, scanning electron microscope, powder X-ray diffraction, X-ray photoelectron spectroscopy, energy-dispersive spectrometer and Raman spectra. According to the results, samarium was doped into the lattice successfully. The as-prepared samples were dispersed well and the average diameter was 60 nm. It showed better catalytic performance than pure ceria and the most appropriate concentration of doping was found.

Keywords. Nanomaterial; hydrothermal method; characterization; CO oxidization; one-step synthesis.

1. Introduction

The study of samarium-doped cerium oxide (SDC) has been flourishing since its excellent electric properties were discovered in the 1980s.¹ At present SDC is applied widely as electrode materials of solid oxide fuel cells (SOFCs) and catalyst of oxidation reactions.² It has been reported that SDC improves the conductivity of electrode,^{3,4} decreases the work temperature of battery^{4,5} and increases the carbon-tolerance ability of the electrodes.⁶ All these properties make SDC to become an ideal material for electrodes. Moreover, it shows excellent catalytic performance in many important organic reactions, such as benzyl alcohol oxidation⁷ and allylic oxidation of cyclohexene.⁸ While CO oxidation is a crucial inorganic reaction in environmental protection, the traditional cerium catalyst, such as gold–palladium-supported nanoparticles⁹ and palladium-supported nanowires,¹⁰ is expensive to spread their applications and it is useful to study the catalytic performance of CO oxidation of SDC, which is effective and more economic.

So far various methods have been used for doping samarium to cerium oxide. Co-precipitation and hydrothermal method are used for preparing nanoscale SDC such as nanorods,¹¹ nanowires,¹² nanoparticles,⁸ while the procedure of synthesis was complicated and not suitable for industrial manufacture. Hence it still remains challenging to establish a one-pot facile synthesis for the preparation of doped ceria with uniform size and shape. In our current work, a series of Sm^{3+} -doped CeO_2

nanospheres have been first prepared via a one-step, mild and environmental-friendly hydrothermal process and the products have better catalytic performance and a large surface.

2. Experimental

2.1 Materials

Cerium(III) chloride heptahydrate [$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, $\geq 99.99\%$] was purchased from Aladdin Industrial Inc. Samarium(III) oxide (Sm_2O_3), polyvinylpyrrolidone (PVP, K30), potassium chlorate (KClO_3), N,N-dimethylformamide (DMF), hydrochloric acid (HCl , 36.0–38.0%) were obtained from Sinopharm Chemical Reagent Co. Ltd. All the above reagents were of analytical grade and were used without further purification. Deionized water was used throughout. HCl solution with a concentration of 1 M was obtained by diluting commercial HCl solution (HCl , 36.0–38.0%).

2.2 The synthesis of Sm^{3+} -doped CeO_2 nanoparticles (P_1 – P_6)

In total, 0.15 g of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, different masses (0.01, 0.02, 0.03, 0.04, 0.05, 0.06 g) of Sm_2O_3 , 0.178 g of PVP and 0.250 g KClO_3 were dissolved in 16 ml of deionized water under vigorous magnetic stirring. Then HCl (1 M) was added into the solution under vigorous magnetic stirring until pH of solution is about 3. Then 0.6 ml of N,N-dimethylformamide was added into the solution under continuous stirring for 15 min. The as-formed solution was transferred into a Teflon-lined autoclave of 20 ml

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capacity and heated for 4 h at 180°C. After the autoclave was cooled to room temperature naturally, light yellow products were collected and washed with deionized water for three times. Finally, the products were washed with absolute ethanol three times and dried in an electric oven at 60°C overnight, and then calcined at 300°C for 200 min. The above products with different Sm^{3+} doping concentrations were labelled as P_1 – P_6 samples.

2.3 Characterization

The phase purity of the sample was examined by X-ray diffraction (XRD) with a Bruker D8 Advance X-ray diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 0.15418$ nm) in the 2θ range from 10° to 80°. The microstructure and morphology of the products were characterized using a transmission electron microscope (TEM, JEM 100-CXII, 80 kV), a high-resolution transmission electron microscope (HRTEM, JEM-2100, 200 kV) and a field-emission scanning electron microscope (FE-SEM, Hitachi, S4800) equipped with an energy-dispersive X-ray spectrometer (EDS). X-ray photoelectron spectra were recorded with a PHI 5300 X-ray photoelectron spectrometer with a standard $\text{AlK}\alpha$ source. The charging of the samples was corrected by referencing all of the energies to the C 1s peak energy set at 284.7 eV, arising from the aliphatic hydrocarbon (C–C) chains. Raman data were obtained using a Horiba Jobin Yvon HRT800 spectrometer with an inverted microscope, using a 633 nm laser line as an excitation source. N_2 adsorption–desorption isotherms were measured with a Quadra-Sorb S1 apparatus at 77 K. The surface areas were calculated by the Brunauer–Emmett–Teller (BET) method, and the pore size distribution was calculated from the desorption branch using the Barrett–Joyner–Halenda (BJH) theory.

2.4 Measurement of catalytic activity

The catalytic activity of the as-obtained samples was evaluated by a continuous flow fixed-bed microreactor operating under atmospheric pressure. In a typical experiment, catalyst particles (50 mg) were placed in the reactor. The reactant gases (1% CO , 10% O_2 and 89% N_2) passed through the reactor at a rate of 60 ml min^{-1} . The composition of the gas exiting the reactor was analysed with an online infrared gas analyzer (Gasboard-3121, China Wuhan Cubic Co.), which simultaneously detects CO and CO_2 with a resolution of 10 ppm. The results were further confirmed with a Shimadzu gas chromatograph (GC-14).

3. Results and discussion

The phase purity of the product was examined by the XRD pattern. Figure 1 shows the typical diffraction

Figure 1. XRD patterns of the as-obtained samples with different Sm-doped amounts: P_1 (0.01 g), P_2 (0.02 g), P_3 (0.03 g), P_4 (0.04 g), P_5 (0.05 g) and P_6 (0.06 g).

patterns of the as-prepared CeO_2 products, including the series of Sm^{3+} -doped CeO_2 samples (P_1 – P_6). The diffraction peaks of all the products illustrated that they can be well indexed to a pure phase of face-centred cubic ceria structures (JCPDS no. 34-0394). Moreover, the diffraction peak of Sm_2O_3 did not appear, which means instead of form binary metal oxide with CeO_2 , the Sm^{3+} is doped into CeO_2 lattice. Furthermore, it can be noticed that the peaks of P_1 and P_2 are much higher and narrower than the peaks of P_3 – P_6 , which means nanospheres of P_1 and P_2 are more regular than that of P_3 – P_6 and the particle diameter of P_3 – P_6 are smaller and have a broader distribution.¹³

The morphology and structures of the as-prepared P_1 – P_6 samples are explored by transmission electron microscopy (TEM). The TEM image (figure 2) shows the products consist of well-dispersed uniform nanospheres with a narrow size range, and the average diameter of the spheres is 60 nm. The boundaries of the nanospheres are smooth and well formed. As the doping amount increase, the size of the nanospheres become smaller (from 50 to 70 nm) and the structure of them become looser and more regular because the colour of TEM images become lighter and more homogeneous. It is because that Sm^{3+} disturbed the crystallization of cerium oxide and cause more defect on the grain boundary as mentioned above.

The phenomenon that the XRD peaks of P_1 and P_2 are much higher and narrower than the peaks of P_3 – P_6 can also be supported by the TEM images (figure 2). It can be easily observed from the images that P_1 and P_2 are made of solid nanospheres with clear boundaries, while the nanospheres of P_3 – P_6 were loose packed and no obvious boundaries could be observed. It may be resulted from that samarium ion doping inhibited the phase transformation from amorphous to fluorite crystals in the solid¹³ and the crystal defects become more severe as the amount of Sm^{3+} grow.

Figure 2. (a–f) TEM images of P_1 – P_6 samples.

The polycrystalline properties provided by the selected area electron diffraction (SAED) patterns from the HRTEM results of P_3 demonstrate that the products are formed of many small nanoparticles. The interplanar spacing of the two planes is about 0.276 nm (figure 3a), which are comparable to the values of the (200) plane of face-centred phase ceria. The result of scanning electron microscopy (SEM) agreed well with the result of TEM.

Elemental composition of the products was analysed by EDS. From figure 4 several peaks of Ce, Sm and O, respectively, can be seen, and the chemical formulas in this paper are based on the results of EDS test. When Sm_2O_3

was added in the reaction, the rate of Sm in products increased (shown in table 1).

The elementary composition and chemical valence on the surface of the as-prepared P_3 ($\text{Ce}_{0.76}\text{Sm}_{0.24}\text{O}_2$) particulate powders were detected by X-ray photoelectron spectra (XPS). Figure 5a shows the XPS survey spectrum of as-prepared product, which indicate the existence of cerium (Ce 3d_{5/2} and Ce 3d_{3/2}), samarium (Sm 4d_{5/2}) and oxygen (O 1s) elements. The carbon peak mainly originates from organic molecules adsorbed on the sample surface. The XPS spectrum of Ce 3d (figure 5c) shows two characteristic peaks of Ce 3d_{3/2} and Ce 3d_{5/2}, which are in agreement with a previous report on Ce^{4+} ion.^{14,15}

Figure 3. (a) HRTEM and (b) SEM images of P₃.

Figure 4. EDS patterns of P₁, P₃ and P₅.

Table 1. Elemental composition of P₁–P₆.

Atomic percent	Ce	Sm	O
P ₁ (Ce _{0.9} Sm _{0.1} O ₂)	21.62	2.55	75.83
P ₂ (Ce _{0.85} Sm _{0.15} O ₂)	32.60	5.98	61.41
P ₃ (Ce _{0.76} Sm _{0.24} O ₂)	24.48	7.65	67.87
P ₄ (Ce _{0.72} Sm _{0.28} O ₂)	19.50	7.58	72.92
P ₅ (Ce _{0.73} Sm _{0.27} O ₂)	24.82	9.39	65.80
P ₆ (Ce _{0.7} Sm _{0.3} O ₂)	23.49	10.08	66.43

As shown in figure 5d, the two peaks correspond to the characteristic Sm 3d_{5/2} and Sm 3d_{3/2} signals.^{16–18} No evidence of other oxidation states of samarium was found.¹⁹ But the binding energy for Sm 3d_{5/2} is 1083.4 eV in Sm₂O₃ (Sm–O bonds),¹⁷ which is little different from Sm 3d_{5/2} in P₃. This phenomenon indicated that the chemical environment surrounding samarium had changed a little because of the doping.²⁰ These results suggest that cerium atoms have been partly substituted by the doped Sm³⁺. In the O 1s XPS spectrum (figure 5b), the main

peak centred at 529.05 eV can be indexed to the lattice oxygen in crystalline CeO₂. The shoulder peak at around 531.35 eV corresponds to the appearance of defective oxygen regions or adsorbed oxygen, indicating a better capacity for oxygen storage, which is also known to be related to the activity of oxidation reaction.²¹

Raman scattering is used to study doping effects on doping nanomaterial. Figure 6 shows the Raman spectra of P₁–P₆. For pure ceria, strong band at 460 cm^{−1} is due to the F_{2g} vibration of CeO₂ fluorite-type lattice.^{22–24} Compared with the pure ceria, the doped ceria have the following characters: the peaks have negative frequency shift and become less symmetric, while their intensity change as the doping amount increase. The red shift and increasing width of peaks of P₁–P₆ are due to the lattice defects,^{25–27} which consist of oxygen vacancies and the dilation of the lattice and different doping amount cause different red shifts. The tendency concluded from figure 6 is that the peak values first decrease, and then increase as the Sm³⁺ doping concentration increase. It

Figure 5. XPS pattern of P_3 ($Ce_{0.76}Sm_{0.24}O_2$): (a) survey spectrum, (b) O 1s, (c) Ce 3d and (d) Sm 3d.

Figure 6. Raman spectra of P_1 – P_6 .

was noticed that the product with highest peak shift is P_3 , and it also has the most intensive broad double peaks around 552 and 603 cm^{-1} . There is a positive correlation between the intensity of these peaks and the amount of oxygen vacancies,²³ hence it can be deduced that P_3 has the most oxygen vacancies. This means the outstanding catalytic performance is not only because of the surface area, but also the oxygen vacancies. Also, it is found that there is an overtone band at around 1080 cm^{-1} in Raman

spectra, which is due to the second-order longitudinal optical (2 LO) mode.^{28,29} The 2 LO band activation is due to the multiphonon relaxation by the resonance Raman effect.³⁰ As for the decreasing intensity of the peaks, it is because of the heavier yellow of the products as the doping amount increase.²³

The nitrogen sorption measurement was performed to further the research on the porous structure of P_3 (shown in figure 7). The adsorption isotherm in the low-relative-pressure region is attributed to the surface area of the nanospheres, whereas the hysteresis loops are from the narrow pores inside the nanospheres, which may result from structure distortion of microspheres caused by Sm doping. The BET surface area of P_3 spherical aggregates was calculated to be 96.241 $m^2 g^{-1}$. The corresponding pore size distribution curve calculated from the desorption branch by the BJH method demonstrates that most of the pore diameters range from 0 to 4 nm.

4. Catalytic performance

Ceria has been widely used as a three-way catalyst in automobile exhaust systems for its high oxygen storage capacity and it is widely accepted that the catalytic processes is mainly related to the adsorption and desorption of gas molecules on the surface of catalyst. The dope of Sm^{3+} , which has the similar radius as $Ce^{3+/4+}$ but

Figure 7. N₂ adsorption-desorption isotherms of P₃. Inset is the corresponding BJH pore size distribution curve.

Figure 8. Catalytic performance of products with different doping amounts.

different valence, can cause lattice defect, thus enhance the oxygen storage capacity and improve the catalytic performance. The products with different doping amounts were evaluated for their catalytic activity towards CO oxidation reaction. Compared with traditional cerium catalyst, the Sm-doped cerium oxides have better catalytic performance for their lower catalytic temperature, especially the P₃ (Ce_{0.76}Sm_{0.24}O₂). The conversion rate of commercial ceria has failed to reach 40% at 300°C,^{24,31} while all products have achieved at least 70% and the P₃ has achieved full conversion. Due to the large surface area P₃ can provide more active sites for conversion, which can be one of the results of high catalytic performance. Figure 8 shows the catalytic performance of P₁–P₆, respectively, and it is seen that the performance becomes better from P₁ to P₃, but worse then. This phenomenon can be supported by Raman spectra, and explained that the P₃ has the most lattice defect, which is in favour of the adsorption and desorption of gas molecules on the surface of catalyst.

5. Conclusion

In summary, a series of Sm³⁺-doped CeO₂ nanospheres by a one-step hydrothermal method was obtained. The morphology and structures of products change as the doping amount increases and so does the catalytic performance. The samarium was doped into the ceria lattice successfully. The Ce_{0.76}Sm_{0.24}O₂ has the best catalytic performance among the series of product as it has the most oxygen vacancies and large surface area. As a catalyst with lower cost and better catalytic efficiency, the samarium-doped nanocerium oxide has potential applications for CO oxidation.

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