



Original Research Paper

Formation of cerium carbonate hydroxide and cerium oxide nanostructures by self-assembly of nanoparticles using surfactant template and their catalytic oxidation



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ABSTRACT

Cerium carbonate hydroxide nanostructures composed of nanoparticles were synthesized using amine surfactant in hydrothermal solution. The nanostructures of the obtained samples were greatly influenced by laurylamine (LA) concentration. The shape of nanostructures of the cerium carbonate hydroxide was maintained after thermal decomposition to CeO₂. A formation strategy is proposed by self-assembly of nanoparticles through surfactant-assisted approach. The obtained CeO₂ nanostructures possess rod-like shape, large pore volumes and high surface areas in synthesis condition of high LA concentration even after thermal treatment at 550 °C. Owing to their unique nanostructure composed of nanoparticles, improved catalytic soot oxidation at lower temperature was achieved as compared with CeO₂ synthesized without surfactant and CeO₂ rod crystals synthesized by a conventional hydrothermal method.

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1. Introduction

Cerium oxide and cerium based materials have attracted much attention in environmental and energy-related applications such as three-way catalysts for auto exhaust gases [1], the water-gas shift reaction [2,3], alcohol stream reforming [4], CO oxidation [5–8], NO reduction [9], and soot oxidation [10–15]. The features of the cerium oxide and cerium based materials in these applications are mainly the result of a combination of its high oxygen-storage capacity, coupled with its ability to change easily between the reduced and oxidized states ($\text{Ce}^{3+} \leftrightarrow \text{Ce}^{4+}$). The oxygen-storage capacity of cerium oxide is often improved by morphology control such as the formation of cubic and rod crystals with specific surface crystallographic facets [2,5–8,15,16]. However, a major problem is its low thermal stability which induces significant decrease of surface area [9,15].

Cerium carbonate hydroxide is a promising precursor to synthesize CeO₂ nanostructures through thermal decomposition because cerium carbonate hydroxides have a potential to possess different unique morphologies and optical properties [17–22]. The obtained CeO₂ nanostructures are also expected to have applications in catalytic oxidation [4,14] because of their potentially thermal stabilities, large porosities and large numbers of oxygen vacancies formed in this synthesis route. For example, Sun et al. [4] have synthesized flowerlike CeO₂ microspheres with hollow structure from CeOHCO₃ via a metamorphic reconstruction and mineralization under hydrothermal condition, which resulted in a good catalytic property and hydrothermal stability for ethanol stream reforming. Thus the catalytic performances of CeO₂ synthesized from cerium carbonate hydroxide strongly depend on the nano- and meso-scale structure. We believe that such an effective structural design of CeO₂ nanostructure prepared from cerium carbonate hydroxide would enhance their structural, redox, and catalytic properties and lead to their wider application. However, little attention has been paid to a relationship between a formation process which affects directly the obtained CeO₂ nanostructure and its catalytic property. Although various CeO₂ supported metal or metal oxide has been often used for catalytic oxidation, an evaluation of CeO₂ nanostructures without metal additives is needed to clarify the effects of the

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nanostructures because many factors such as structural changes and redox properties induced by metal additives influence the catalytic performance [11]. A comparison of the catalytic properties between CeO₂ crystals with specific surface crystallographic facets and CeO₂ nanostructures prepared from cerium carbonate hydroxide is also an interesting issue, but the comparison has not been studied yet.

Here, we report a synthesis of cerium carbonate hydroxide nanostructures consisting of nanoparticles using laurylamine (LA) in hydrothermal solution. The nanostructures of the obtained samples were greatly influenced by LA concentration. The shape of nanostructures of the cerium carbonate hydroxide was maintained after thermal decomposition to CeO₂. A formation strategy is proposed by self-assembly of nanoparticles through surfactant-assisted approach. The obtained CeO₂ nanostructures formed by self-assembly of nanoparticles were used as catalysts for soot oxidation as it is an important catalytic oxidation for removal of atmospheric pollutants. This was done to demonstrate and compare their catalytic activity with CeO₂ synthesized without surfactant and CeO₂ rod crystals with specific surface crystallographic facets synthesized according to published procedures.

2. Materials and methods

2.1. Synthesis of cerium carbonate hydroxide and cerium oxide nanostructures

All the chemicals are in analytical grade of over 99% purity from Wako Pure Chemical Industries. Ce(NO₃)₃·6H₂O (2.17 g) was mixed with 1 M (NH₄)₂CO₃ solution (50 mL). LA aqueous solutions (80 mL) of various concentrations were added to the mixed solution. The LA/Ce(NO₃)₃·6H₂O molar ratio (*R*) was controlled to 0, 1, 3, and 6 by changing the LA concentration. The pH was adjusted to 9.5 by adding aqueous NH₃. The mixed solution was transferred to a Teflon autoclave, aged at 100 °C for 24 h, and kept at 140 °C for 96 h. After washing with distilled water and 2-propanol, the product was centrifuged and dried at 60 °C in air. The obtained sample was calcined at 550 °C for 5 h. The obtained sample is denoted by Ce-LA-*R*. The sample synthesized without LA is denoted by Ce-no amine.

For comparison, CeO₂ rod crystals was synthesized by a conventional hydrothermal method based on the published procedures [15,16]. CeCl₃·7H₂O (1.86 g) were dissolved in 40 mL of distilled water. After stirring for 30 min, 10 M NaOH aqueous solution (40 mL) was added to the CeCl₃ solution. The mixed solution was transferred to a Teflon autoclave, aged at 100 °C for 24 h, and kept at 140 °C for 96 h. After washing with distilled water, the product was centrifuged and dried at 60 °C in air. The obtained sample was calcined at 550 °C for 5 h in order to compare the thermal stability with the obtained cerium oxide nanostructures as mentioned above. The CeO₂ rod crystals were denoted by EX-Ce-rod.

2.2. Characterization of the samples

The crystalline phases of the samples were identified using powder XRD (RINT2500X, Rigaku Corp.) with monochromatized Cu K α radiation at 40 kV and 40 mA. TEM images of the samples were recorded using a JEM-2100F instrument (JEOL Ltd.). TG was performed using a TG/DTA 6300 apparatus (SII Nanotechnology Inc.), at a heating rate of 10 °C min⁻¹ under flowing air. Specific surface areas were calculated from adsorption isotherms obtained using a conventional BET N₂ adsorption apparatus (BELSORP-18SP, Bell Japan Inc.). The redox behaviors of the samples were investigated using H₂ temperature-programmed reduction (H₂-TPR) (BELCAT, Bell Japan Inc.) The sample (50 mg) was fixed in a quartz

U-tube reactor. The rate of H₂ consumption was measured using a thermal conductivity detector with 5% H₂/Ar at a heating rate of 10 °C min⁻¹ in the temperature range from 100 to 800 °C. XPS was performed with a PHI5000 VersaProbe II high-performance electron spectrometer (ULVAC-PHI Inc.) using monochromatic Mg K α radiation (1253.6 eV) and operated at an accelerating voltage of 15 kV. All binding energies were referenced to adventitious C 1s at 284.6 eV.

2.3. Catalytic oxidation procedure

Soot oxidation was investigated using commercially available carbon black (CB) powder as a soot particle mode. The catalytic tests were performed using TG analysis. CB and the calcined sample at a weight ratio of 1/4 [10,11] were ground using an agate mortar and pestle for 10 min to obtain a tight contact mixture. The mixture of CB and the calcined sample was treated at 300 °C for 1 h in a N₂ atmosphere and then heated from 200 to 700 °C in air at a constant rate of 5 °C min⁻¹. The *T*_{ig} and *T*_{max} values were determined from the TG and DTA curves.

3. Results and discussion

3.1. Synthesis of cerium carbonate hydroxide and cerium oxide nanostructures

The cerium carbonate hydroxide was synthesized using Ce(NO₃)₃·6H₂O as a cerium source, (NH₄)₂CO₃ as an alkali and carbon source. The effects of LA concentration on the crystal structures and shapes of the cerium carbonate hydroxide were investigated by XRD, SEM and TEM.

Fig. 1 shows XRD patterns of dried samples synthesized at various *R* values. In the absence of LA (*R* = 0), all the peaks can be indexed to the hexagonal phase of CeCO₃OH (JCPDS 32-0189). At *R* = 1, the crystal structures of the CeCO₃OH hexagonal phase and

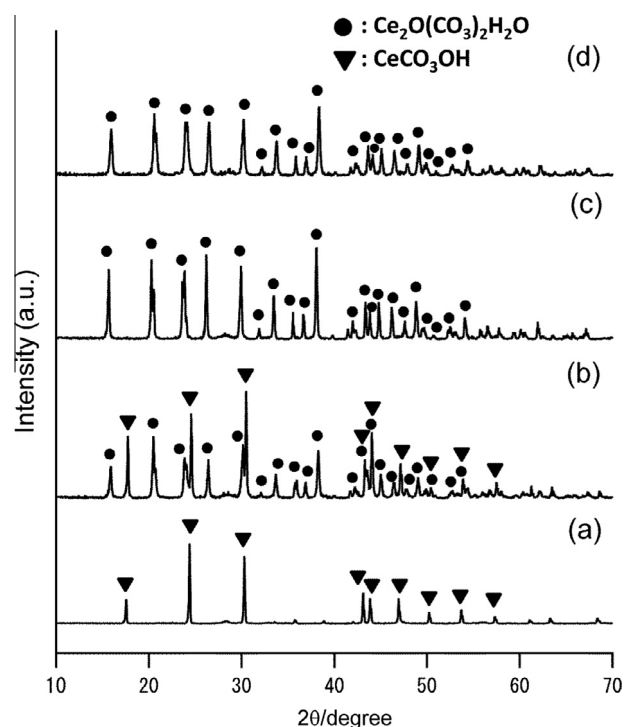


Fig. 1. XRD patterns of dried samples synthesized at (a) *R* = 0, (b) *R* = 1, (c) *R* = 3, and (d) *R* = 6.

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