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Template-free controlled hydrothermal synthesis for monodisperse flowerlike porous CeO_2 microspheres and their superior catalytic reduction of NO with NH_3

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ABSTRACT

Monodisperse flowerlike porous CeO_2 microspheres with the diameters of 2–5 μm composed of numerous nanosheets as the petals with variable thickness of 40–200 nm have been successfully synthesized via a facile hydrothermal technique. Various techniques have been applied to investigate the CeO_2 nanostructures, including XRD, SEM, TEM, XPS, Raman spectra, PL spectra, BET, and in situ DRIFTS. The reaction temperature, reaction time, reaction solution, the amount of H_2O_2 and ethylenediamine were systematically investigated. It is found that the reaction temperature, reaction time, reaction solution, the amount of H_2O_2 and ethylenediamine are key parameters for controlling the final morphology. The flowerlike CeO_2 microspheres have a cubic fluorite structure and there are Ce^{3+} ions and oxygen vacancies in surface of samples. The as-synthesized CeO_2 samples showed enhanced optical properties with the decrease of reaction temperature. Furthermore, flowerlike CeO_2 microspheres obtained at 120 °C for 48 h displayed a high surface area of 83.81 $m^2\ g^{-1}$ and narrow pore size of 3.86 nm by N_2 adsorption and desorption measurement. The outstanding catalytic performance for the flowerlike CeO_2 microspheres can be attributed to the much larger surface areas, fancy morphology and the best redox behaviour of surface oxygen on the CeO_2 surface.

1. Introduction

In recent years, there has been growing interest in the controlled synthesis of higher ordered inorganic crystals with specific dimensions and well-defined shapes because of the unique shape-dependent materials properties, which would result in a wide range of electrical, optical, or magnetic properties and open a new domain of theoretical and technological interest [1–3]. In this respect, because of the distinct size and shape, large surface area, abundant active sites and chemical functionality, three dimensional (3D) hierarchical structures built with low dimensional nanostructures (such as nanowires, nanorods, nanotubes, nanosheets and nanobelts) possess the prominent advantages from 2D or 1D micro/nanostructure and can be a promising candidate for many applications. In addition, the porous structure is largely introduced to extend the potential applications of the unique nanomaterials to fields such as versatile catalysts and catalyst supports due to its high surface area and increased dispersion of active secondary components [4]. Therefore, the preparation of 3D micro/nanostructured materials with porous structure has been the subject of intense interest. At present, many efficient strategies have been developed to fabricate the 3D hierarchical structures of various functional materials, such as precursor template synthesis [5], self-assembly of building blocks through hydrophobic interactions [6], fabrication via Kirkendall process [7], oriented aggregation [8], thermal reduction process [9], and thermal oxidation process [10].

As one of the most important rare earth oxides, CeO_2 with remarkable properties due to its abundant oxygen vacancy defects, high oxygen storage capacity and ability to uptake and release oxygen via the transformation between Ce^{3+} and Ce^{4+} has attracted considerable attention in recent years. Therefore, it has been extensively studied and employed in many applications, such as three-way catalysts (TWC) for the elimination of vehicle exhaust

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gases [11], ultraviolet (UV) blocking materials [12], photocatalysts for water oxidation [13], oxygen sensors [14] and oxygen ion conductors in solid oxide fuel cells [15]. Recent advances in the morphology-controlled synthesis of the nanomaterials offer new opportunities of developing novel CeO_2 functional materials with desired structural properties, especially in morphology-dependent catalytic activity. Up to now, numerous morphologies of cerium oxides are synthesized by chemical and physical methods, such as nanospheres [16], nanoflowers [17], nanoplates [18], nanoshuttles [19], nano-octahedrons [20], nanowires [21], nanotubes [22], nanorods [23] and other morphologies [24–26]. Among these nanomaterials, low dimension nanostructures with more active planes [27] or oxygen vacancies [28] are helpful for the catalytic activity. Moreover, nanostructured and porous CeO_2 or CeO_2-based compounds have attracted special attention due to the large specific surface area, the improvement in the redox properties and catalytic performance. Another is the design of 3D hierarchical micro/nanostructured CeO_2 employing the low dimension nanocrystals as the initial building blocks. In this respect, 3D flowerlike CeO_2 structures are also becoming more promising because of their increasing surface area and providing channels for various photochemical reactions [24,29–31]. Although significant progress in the synthesis approaches for 3D flowerlike CeO_2 with hierarchical architectures has been achieved, the higher synthesis cost, larger energy consumption and more complicated manufacturing procedures are unavoidable. In addition, there have a serious obstacle to synthesize 3D flowerlike CeO_2 with hierarchical architectures in solution-phase, because CeO_2 with the cubic structure has no intrinsic driving force for anisotropic growth in aqueous routes. On the other hand, although a number of 3D hierarchical micro/nanostructures have been obtained, the investigation of the relation between different hierarchical structures is still crucial for realizing 3D hierarchical morphology-controlled synthesis. Furthermore, to the best of our knowledge, there is no report on utilizing 3D CeO_2 hierarchical micro/nanostructures as catalyst for degradation of industrial exhaust gas (NO, NH_4).

Herein, we reported facile, smart and low-cost template-free hydrothermal route to synthesize hierarchical and porous CeO_2 nanostructured materials using $CeCl_3 \cdot 7H_2O$ as cerium source, NH_4HCO_3 as precipitator, H_2O_2 as an oxidant and ethanediamine as surfactant. The morphologies of the CeO_2 hierarchical architectures can be controlled by adjusting the temperature and solvent in the hydrothermal system. The various kinds of tunable factors and the possible formation mechanism were investigated in detail. It was inspiring that the as-prepared 3D CeO_2 hierarchical structures exhibit very larger surface area and excellent catalytic performance for catalytic reduction of NO with NH_3, which should make the hierarchical and porous CeO_2 nanostructured materials excellent candidates for applications in the treatment of industrial exhaust gas.

2. Experimental

2.1. Material preparation

All the reagents were of analytical grade purity and used without further purification. In a typical experiment, 4 mmol $CeCl_3 \cdot 7H_2O$ and 50 mmol NH_4HCO_3 were dissolved in 5 and 17 mL deionized water under vigorous stirring until a clear solution was formed, respectively. Then, 17 mL NH_4HCO_3 aqueous solution was rapidly added to 5 mL $CeCl_3 \cdot 7H_2O$ aqueous solution under continuous stirring. Subsequently, the white suspension promptly turned brown after dropwise addition of 3 mL hydrogen peroxide solution, continuous stirring until no bubble, followed by the addition of 10 mL ethylenediamine. Continuous stirring for 1 h before the suspending solution was transferred into a 50 mL Teflon-lined autoclave and heated at 120 °C for 48 h, followed by natural cooling to room temperature. The white precipitates were washed several times with distilled water and absolute ethanol, and then dried at 80 °C for 12 h. The products of others were obtained through a similar procedure except changing a single parameter.

2.2. Characterization

The powder X-ray diffraction (XRD) patterns of the samples were recorded on an X-ray diffractometer (XRD, XD-3) using Cu Kα radiation ($\lambda = 0.154$ nm). Morphologies and sizes of synthesized products were studied by scanning electron microscope (SEM, S-4800, Japan) and transmission electron microscope (TEM, JEM-2100, Japan). Elemental bonding valence was achieved by X-ray photoelectron microscopy (XPS, ESCALAB 250 US Thermo Electron Co). The Raman spectra were recorded by a Raman spectrometer system (inVia-Reflex) using a laser with 532 nm excitation at room temperature. Nitrogen adsorption and desorption isotherms were measured at 77 K using a Micromeritics ASAP 2020 V3.00H system after the samples were first degassed at 100 °C overnight. Specific surface areas were determined by the BET method and the mesopore size distribution was determined by the Barrett-Joyner-Halenda (BJH) method. Photoluminescent (PL) emission spectra were measured by a fluorescence spectrophotometer (Hitachi F-4500) using excitation light of 330 nm. In situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) spectra were recorded on a Fourier transform infrared spectrometer with a gas pool (600FTIR, CAI companies of the United States).

2.3. Catalytic activity test

The catalytic activity of the as-obtained CeO_2 samples was evaluated by a continuous fixed-bed microreactor operating under atmospheric pressure. In a typical experiment, as-prepared CeO_2 samples (1 g) were placed in the reactor. The reactant gases (500 ppm NO, 500 ppm NH_3, 5% O_2, balanced with Ar) were fed into the reactor at a rate of 200 mL min^{-1} and the gas hourly space velocity (GHSV) is 24000 h^{-1}. NO and NO_2 concentration was online monitored by Fourier infrared analyzer equipped with a gas pool (600FTIR, CAI companies of the United States). The data of catalytic activity as a function of temperature were collected at required temperature keeping 15 min when reaction reached a steady state. The catalytic activity can be evaluated in terms of the conversion (Y) of NO_x gas according to the following equation ($NO_x = NO + NO_2$):

$$Y_{NOx} = \{1 - [NO_x]_{out}/[NO_x]_{in}\} * 100\% \tag{1}$$

3. Results and discussion

3.1. XRD characterization

The crystal structure and phase purity of the obtained CeO_2 samples were examined by XRD. Fig 1 shows the XRD patterns of the products obtained at 120 °C, 160 °C, and 200 °C for 48 h. All the detectable peaks can be readily indexed to a pure cubic structure of CeO_2 (JCPDS No. 43-1002, space group: $Fm\overline{3}m$) and no signals of impurities corresponding to the $Ce(OH)_3$ or $CeOHCO_3$ were observed in Fig 1. It can be obviously seen that all the diffraction peaks are sharp but broad, which indicate as-obtained CeO_2 samples are composed of primary small crystal particles and possess a good crystallinity.