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Diameter-dependent catalytic activity of ceria nanorods with various aspect ratios for toluene oxidation

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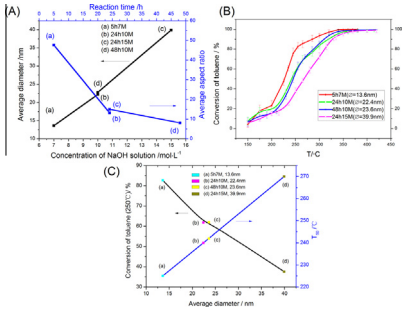
HIGHLIGHTS

- Ceria nanorods with various aspect ratios were synthesized controllably.
- The relationship between diameter of nanorod and alkali concentration was found.
- The influence factors on the length of nanorods were also discovered.
- A high correlation between removal of toluene and diameter of nanorod was verified.
- The most active nanorods proved to be very stable during the toluene oxidation.

GRAPHICAL ABSTRACT



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ABSTRACT

Ceria nanorods with various aspect ratios were successfully synthesized by a convenient hydrothermal method without any templates or surfactants. The samples were characterized by TEM, HRTEM, XRD, N_2 adsorption/desorption, XPS, Raman and H_2-TPR. The results showed that the diameter and length of the ceria nanorods were determined by the concentration of NaOH solution and the hydrothermal reaction time, respectively. In addition, the diameter-dependent catalytic activity for abatement of toluene had been found over the nanorods with various aspect ratios. The thinner nanorods presented higher catalytic activity owing to the existence of more Ce^{3+} ions and more oxygen vacancy sites on the surface. Over the thinnest nanorods, the most active catalyst, three consecutive runs in toluene oxidation and a longstanding oxidation test running at 380 °C for 100 h were also carried out.

1. Introduction

As one of the most important rare-earth metal oxides, CeO_2 nanomaterials have been paid much attention, because of their wide range of applications such as oxygen sensors, irradiation protectors and environmental catalysts for catalytic removal of NOx, CO and volatile organic compounds (VOCs) [1–3]. CeO_2 nanomaterials with different shapes including nanorods, nanotubes, nanocubes and nanowires have been fabricated successfully. At present, most of the researches were focused on the synthesis and morphology-sensitive catalytic activities of ceria nanomaterials with different shapes. Zhou et al. [4] demonstrated that ceria nanorods with well-defined crystal planes were more reactive than nanoparticles for CO oxidation. Tana et al. [5]

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studied the morphology-dependent redox and catalytic properties for CO oxidation over ceira nanowires, nanorods and nanoparticles. This revealed that ceria nanorods gave higher oxygen storage capacity and catalytic activity than nanoparticles, and nanowires exposed a larger proportion of active planes on the surface. Dai et al. [6] investigated the catalytic oxidation of 1,2-dichloroethane and ethyl acetate over ceria nanorods, nanocubes and nano-octahedrons, and found that ceria nanorods showed the highest catalytic activities, followed by nanocubes and nano-octahedrons. In view of these, ceria nanorods were generally confirmed to be reactive in catalytic reactions. However, the control of the micro appearance of the rod-shaped ceria have not been got noticed extensively.

Some reports [7–9] have presented the controlled synthesis of high-aspect-ratio gold or silver nanorods, as well as the metal oxides nanorods, such as TiO_2 [10], SnO_2 [11] and ZnO [12] nanorods. It was generally accepted that dissolution/recrystallization mechanism was applicable to formation of ceria nanostructures under hydrothermal methods [13]. When the dissolution/recrystallization rate was fast enough under the high concentration of NaOH solution, $Ce(OH)_3$ nuclei grew anisotropically, resulting in the formation of CeO_2 nanorods. Murciano et al. [13] proposed that the diameter and length of the CeO_2 nanorods increased as the temperature and alkali concentration increased. Ahniyaz et al. [14] found that the CeO_2 nanorods were slowly and selectively shortened with time but without any change of the rod diameter through the dissolution process in the presence of the surfactant. It was well-understood that alkali concentration, time and temperature of synthesis can influence the diameter or length of ceria. However, there is no any literature reporting the relationship between the diameter of nanorods and their catalytic activity. Therefore, the aims of this work were to synthesize the ceria nanorods with aspect ratios, to systematically analyze the catalytic activities of ceria nanorods in toluene oxidation, and to examine the correlation between the diameter of nanorods and the catalytic activity.

In the present work, CeO_2 nanorods with various aspect ratios were controllably synthesized without any templates or surfactants. The length and diameter of CeO_2 nanorods could be controlled by tuning the hydrothermal reaction time and the concentration of NaOH solution. Also, a high correlation between the catalytic activity for toluene oxidation and diameter of nanorods had been demonstrated. Over the most active catalyst, three consecutive runs in the toluene oxidation and the longstanding test were both performed. The catalyst proved to be perfectly stable.

2. Experimental

2.1. Synthesis of ceria nanorods

All chemicals were analytical reagents without further purification. In a typical procedure, cerium acetate ($Ce(CH_3COO)_3{\cdot}nH_2O$) (5 mmol) was dissolved in deionized water (20 mL), followed by adding NaOH solution (55 mL). The mixed solution was transferred into a Teflon-lined stainless steel autoclave (100 mL) and then kept at 130 °C for some time. The as-synthesis samples were put into the ultrasonic bath at room temperature for 2 h. Finally, the precipitate was washed with deionized water and then dried at 100 °C for 24 h. The samples were named according to the synthetic conditions, the hydrothermal reaction time and the concentration of NaOH solution. To confirm the diameter and length as a function of the synthetic conditions including hydrothermal reaction time (5, 24, 48 h) and concentration of NaOH solution (7, 10, 15 mol L^{-1}), a series of experiments was carried out.

2.2. Characterization

XRD patterns were performed on a D8 ADVANCE diffractometer (Bruker, Germany) with CuKα radiation (40 kV, 40 mA, scanning step = 0.02°, λ = 0.154056 nm). TEM and HRTEM images were obtained on JEM-2100HR (JEOL, Japan). Surface areas were measured on an ASAP2020M analyzer (Micromeritics, USA). Before measurement, the samples were outgassed at 100 °C in vacuum for 4 h. The BET method was used to calculate the surface areas of samples. The XPS spectra were acquired on a Kratos AXIS Ultra DLD photoelectron spectrometer (Shimadzu, Japan). The pass energy was 40 eV. Charge effects of samples were corrected by setting the binding energy of adventitious carbon (C1s) at 284.6 eV. Raman spectra were recorded by a LabRAM Aramis laser Raman spectrometer (HYJ, France) at an excitation laser wavelength of 532 nm. H_2-TPR was measured by Auto Chem II Chemisorption Analyzer (Micromeritics, USA). Samples (100 mg) were pretreated in Ar at 300 °C for 30 min. After the samples were cooled down to 60 °C, 10% H_2/Ar mixture gas was inlet and the reactor was heated at a rate of 10 °C min^{-1} to 850 °C.

2.3. Catalytic performance evaluation

Toluene was chosen as the representative environmental pollutant. Catalytic activity evaluation for toluene oxidation was carried out in a conventional continuous flow micro-reactor made of a quartz tube of 8 mm inner diameter at the temperature range of 150–420 °C. Catalysts (300 mg) were packed at the bed of the reactor. Before the activity evaluation, the catalysts were heated with 20% O_2 at 350 °C for 60 min. The feed flow through the reactor was set with toluene (1000 ppm), which was delivered by dry air (20% O_2, 150 mL min^{-1}), and the weight hourly space velocity at 32000 ml g^{-1} h^{-1}. Quantitative analysis of toluene was analyzed at a given temperature for 8 times by on-line GC-2014C (Shimadzu, Japan) equipped with FID. The conversion of toluene (X) was calculated as $X = (1 - C_{toluene}/C_{toluene,in}) \times 100\%$, where $C_{toluene}$ is the concentration of toluene at steady state; $C_{toluene,in}$ is the inlet concentration of toluene.

2.4. Stability test

Three consecutive runs in toluene oxidation were performed as follows: introduction of the gas mixture at room temperature, heating at a rate of 1 °C min^{-1} up to 400 °C, then cooling down. This procedure was repeated three times. To detect the concentration of CO_2, a nickel catalyst converter was placed before the FID and used for converting carbon oxides quantitatively into methane. The yield of CO_2 (Y) was calculated as $Y = [C_{CO_2}/(7 \times C_{toluene,in})] \times 100\%$, where C_{CO_2} is the concentration of CO_2 at steady state.

A longstanding toluene oxidation test was performed over the most active ceria nanorods at 380 °C for 100 h. The gas mixture was introduced and heated at a rate of 1 °C min^{-1} up to 380 °C, then the catalyst was run for 100 h maintaining the temperature constantly.

3. Results and discussion

3.1. Synthesis of ceria nanorods with various aspect ratios

Different concentrations of NaOH solution were used to discuss the correlation between the diameter of nanorods and the alkali concentration. The diameter distribution of nanorods of each sample in the TEM images (Fig. 1(e–h)) was shown in Fig. 1(i). As exhibited in Fig. 1(a–d), increasing diameters of nanorods with increasing concentration of NaOH solution could be observed.