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Morphology and crystal-plane effects of Zr-doped CeO_2 nanocrystals on the epoxidation of styrene with tert-butylhydroperoxide as the oxidant

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ABSTRACT

The morphology effect of Zr-doped CeO_2 was studied in terms of their activities in the selective oxidation of styrene to styrene oxide using tert-butyl hydroperoxide as the oxidant. In the present work, Zr-doped CeO_2 nanorods exhibited the highest catalytic performance (yield of styrene oxide and TOF value) followed by nanoparticles and nanocubes. For the Zr-doped CeO_2 nanorods, the apparent activation energy is 56.3 kJ/mol, which is much lower than the values of catalysts supported on nanoparticles and nanocubes (73.3 and 93.4 kJ/mol). The high resolution transmission electron microscopy results indicated that (1 0 0) and (1 1 0) crystal planes are predominantly exposed for Zr-doped CeO_2 nanorods while (1 0 0) and (1 1 1) for nanocubes, (1 1 1) for nanoparticles. The remarkably increased catalytic activity of the Zr-doped CeO_2 nanorods is mainly attributed to the higher percentage of Ce^{3+} species and more oxygen vacancies, which are associated with their exposed (1 0 0) and (1 1 0) crystal planes. Furthermore, recycling studies proved that the heterogeneous Zr-doped CeO_2 nanorods did not lose its initial high catalytic activity after five successive recycles.

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1. Introduction

Epoxidation reaction of styrene plays an important role in industrial processes because the products from epoxidation reaction of styrene are versatile intermediates in fine chemicals for the synthesis of perfumes, plasticizers, pharmaceuticals and drugs, etc. [1]. Traditionally, the epoxidation of styrene is carried out by the direct oxidation of alkenes with stoichiometric peracids which produced much waste and byproducts, and even worse, the peracids are corrosive, hazardous to the environment. With growing attention paid to the sustainable development, much more efforts have been made to develop a variety of new processes of styrene epoxidation using H_2O_2, urea-H_2O_2 or TBHP as oxidants with the catalysts such as TS-1 [8], Ti-SiO_2 [9], Ti-HMS [10], as well as γ-Al_2O_3 [11]. Meanwhile, the separable solid catalysts, such as Mo [2], Fe [3], Mn [4], Co [5], Cu [6] and Ni [7] based catalysts, were proven to be efficient in the epoxidation of styrene. However, the catalysts mentioned above exhibited comparatively unsatisfied epoxide selectivity or low activity [8–11].

As a well-known functional rare earth material, ceria has been widely applied in the fields of industrial heterogeneous catalysts, such as automotive three-way exhaust (TWCs) [13], water-gas-shift (WGS) reactions [14], solid oxide fuel cells anodes (SOFCs) [15]. In order to promote the physical and chemical properties of CeO_2, incorporation of cheaper transition metals such as Mn, Fe, Co, Ni, and Zr by doping approach is a suitable option because of the low cost and strong stability of transition metals against poisoning. For example, recently, Chen et al. [16] reported the shape effect of $Ce_{1-x}Zr_xO_2$ nanorods in terms of redox features and catalytic activity in CO oxidation. Besides, other groups reported that CeO_2–CuO nanomaterials showed high catalytic activity when compared with pure CeO_2 [17]. The insertion of Zr into ceria lattice leads to structural distortions of the cubic fluorite lattice compared with pure CeO_2, ultimately resulting in the enhancement of mobility of lattice oxygen and the density of oxygen vacancies. CeO_2 in a cubic fluorite structure possesses three low-index planes: (1 1 0), (1 1 1) and (1 0 0); the (1 1 1) plane is the most stable, followed by (1 1 0) and (1 0 0) facets [18–20]. As we know, ceria catalysts with different morphologies were established to possess different crystal planes and surface properties [21], which can influence the interaction between ceria surface and the adsorbed reactants. For instance, Zhou et al. found that CeO_2 nanorods showed better

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catalytic performance in CO oxidation than irregular nanoparticles because of the exposed reactive crystal planes [18]. Moraes et al. reported the effects of ceria morphology on catalytic performance of Ni/CeO_2 for the low temperature steam reforming of ethanol and found that Ni supported on ceria nanocubes had the best performance [22]. Fan et al. found that spindle-like CeO_2 showed a higher catalytic activity on CO conversion [23]. So far, the morphology dependence on Zr-doped CeO_2 nanomaterials for the epoxidation reaction of styrene has been rarely reported yet.

In our previous work, the CeO_2 nanorods with various Zr dopant concentrations catalysts are prepared and investigated in terms of their catalytic activities in catalyzing styrene oxidation [24]. In the present work, Zr-doped CeO_2 catalysts of different morphologies are further investigated in terms of their activities in catalyzing the styrene oxidation reaction. The structure of the Zr-doped CeO_2 is studied using various techniques including Brunauer–Emmett–Teller (BET) method, X-ray diffraction (XRD), transmission electron microscopy (TEM), high-resolution transmission electronmicroscopy (HRTEM), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS) in order to investigate the relationship between the morphology and the catalytic activity. It is found that the morphology has a great influence on the exposed crystal planes, oxygen vacancy concentrations and the content of Ce^{3+} ions, which contribute to the variation of the catalytic activity in styrene oxidation reaction.

2. Experimental

2.1. Catalyst preparation

All the materials were purchased from Sinopharm Chemical Reagent Co., Ltd. China. All chemicals were used without further purification. Deionized water was used throughout the experiments.

Zr-doped CeO_2 nanorods, Zr-doped CeO_2 nanocubes, and Zr-doped CeO_2 nanoparticles were prepared by a hydrothermal method varying the amount of reactant and hydrothermal temperature. The theoretical molar ratios of Zr/(Zr+Ce) over the Zr-doped CeO_2 were all about 10%. Typically, 4.5 mmol of $Ce(NO_3)_3{\bullet}6H_2O$, 0.5 mmol of $Zr(NO_3)_4{\bullet}5H_2O$, and an appropriate amount of NaOH (19.2 g for nanorods and nanocubes, 0.32 g for nanoparticles) were dissolved into 40 mL of distilled water, respectively. Then, the solution was mixed together and kept stirring for 30 min. The mixture was then transferred to a stainless steel reaction tank with polytetrafluoroethylene (PTFE) lining (100 mL) and maintained at an appropriate temperature (373 K for nanorods, 453 K for nanocubes and nanoparticles) for 24 h. After centrifugation and washing with water and ethanol, the precipitate was dried at 353 K overnight, and finally calcined at 673 K for 5 h in air with the ramping rate of 2 °C/min. The as-prepared Zr-doped CeO_2 nanorods, Zr-doped CeO_2 nanoparticles and Zr-doped CeO_2 nanocubes were respectively denoted as Zr-doped CeO_2 NR, Zr-doped CeO_2 NP and Zr-doped CeO_2 NC.

2.2. Characterizations

XRD patterns were obtained on a Bruker D8 advance spectrometer with Cu $K\alpha$ radiation ($\lambda = 0.154$ nm), operated at 40 mA and 40 kV, respectively. The lattice parameter *a* value was calculated using the Scherrer equation. TEM images were performed on a JOEL JEM 2010 transmission electron microscope. The samples were supported on carbon-coated copper grids for the experiment. XPS was performed using a RBD 147 upgraded Perkin Elmer PHI 5000C ESCA system equipped with a dual X-ray source, of which the Mg $K\alpha$ (1253.6 eV) anode and a hemispherical energy analyzer was used. The background pressure during data acquisition was maintained at $<10^{-6}$ Pa. Measurements were performed at a pass energy of 93.90 eV. All binding energies were calibrated using contaminant carbon (C 1*s* = 284.6 eV). The actual composition of the catalysts was determined by Optima 8000 ICP-OES Spectrometer. The laser Raman experiments were obtained using a Jobin Yvon Dilor Labram I Raman spectrometer equipped with a charge coupled device detector, holographic notch filter, and the He-Ne laser radiating at 632.8 nm. Specific surface areas of the catalysts were measured by nitrogen adsorption-desorption at 77 K (Micromeritics Tristar ASAP 3000) employing the BET method. The sample was pre-treated at 523 K in vacuum for 3 h before test to degas the adsorbed moisture.

2.3. Activity test

The epoxidation of styrene was carried out at reflux oil bath temperature of 353 K in a closed 25 mL regular glass reactor with magnetically stirred (400 r/min) using 70 wt% aqueous *t*-butyl hydroperoxide (TBHP) as the oxidant and acetonitrile as solvent. First, 0.05 g of the catalyst, 8.7 mmol of 70 wt% aqueous TBHP and 10 mL of acetonitrile were introduced into the regular glass reactor at 353 K with magnetic stirring. Then, 4.35 mmol of styrene was added into the above mixture to start the reaction and the mixture was maintained for a period of time. Gas chromatography (GC) was used to carry out the quantitative analysis of the reaction products, and GC-mass spectroscopy (GC-MS) was applied to determine different products in the reaction mixture.

Substrate conversion = moles of substrate converted/moles of substrate used;

Product selectivity = moles of product formed/moles of substrate converted;

The stability was tested as follows: the catalyst was separated by centrifuge, washed by water and ethanol for several times, and dried under 353 K for 12 h.

3. Results and discussion

3.1. Characterization of the as-prepared material

The morphology of the synthesized Zr-doped CeO_2 nanoparticles, Zr-doped CeO_2 nanorods, and Zr-doped CeO_2 nanocubes are investigated by TEM and HRTEM as shown in Fig 1. As presented in Fig 1(a), Zr-doped CeO_2 nanoparticles are uniformly distributed and established to be around 10 nm in diameter. Fig 1(b) depicts a high revolution TEM image of Zr-doped CeO_2 nanoparticles with a fast Fourier transform analysis (inset). According to the HRTEM image, the dominating (1 1 1) planes are observed with an interplanar spacing of 0.32 nm, being accorded well with the previous report [25]. For the Zr-doped CeO_2 nanorods, the measured size is approximate with 30–80 nm in length and 10 ± 1 nm in diameter as shown in Fig 1(c). Meanwhile, (1 0 0) and (1 1 0) crystal planes are predominantly exposed with an interplanar spacing of 0.26 and 0.19 nm according to its HRTEM image. For the Zr-doped CeO_2 nanocubes exhibited in Fig. 1(e) and (f), the diameter distribution is about 60–80 nm. At the same time, a small number of (1 0 0) planes and the dominating (1 1 1) planes are observed with an interplanar spacing of 0.27 and 0.32 nm. Some light points on the ceria are observed from the HRTEM image in Fig. 1(b), (d), (f), revealing the existence of the surface defects. Theoretical studies have shown that (1 1 1) is the least active surface followed by (1 0 0) and (1 1 0), in which the energy needed to produce oxygen vacancy is inverse proportional to the order of the reactivity of crystal planes [26–28]. Thus, according to the exposed crystal planes of Zr-doped CeO_2 of different morphologies observed in HRTEM image, the Zr-doped CeO_2 nanorods exhibited the highest concentration of surface oxygen vacancies, followed by Zr-doped

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