



Morphology effect of Ru/CeO₂ catalysts for the catalytic combustion of chlorobenzene



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ABSTRACT

The present work elucidated the morphology and crystal-plane effects of nanoscale ceria on the activity of Ru/CeO₂ catalysts toward catalytic combustion of chlorobenzene taken as a model of chlorinated aromatic hydrocarbons (CAHs). CeO₂ nanorods (CeO₂-*r*), nanocubes (CeO₂-*c*) and nano-octahedra (CeO₂-*o*) (enclosed by {110} and {100}, {100} and {111}, respectively) as supports, were prepared by wet impregnation. The status and structure of Ru species is quite dependent on the enclosed various facets. Ru/CeO₂-*r* possesses much more Ru⁴⁺, oxygen vacancies and Ru–O–Ce bonds than Ru/CeO₂-*c* and Ru/CeO₂-*o*, indicating that there is a stronger interaction between Ru and CeO₂-*r*. The surface oxygen mobility and reducibility follow the order of Ru/CeO₂-*r* > Ru/CeO₂-*c* > Ru/CeO₂-*o*. The activity test of chlorobenzene oxidation shows that Ru/CeO₂-*r* is more active than that of Ru/CeO₂-*c* and Ru/CeO₂-*o*, with T_{10%} and T_{90%} of 160 and 280 °C, respectively, which can be related to a larger number of Ru–O–Ce bonds, higher content of Ru⁴⁺ and surface oxygen mobility and reducibility. These results confirm that the activity of Ru/CeO₂ catalysts for CB oxidation is greatly affected by CeO₂ shape/crystal plane.

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1. Introduction

CAHs continue to attract considerable public concern because of their persistence in the environment, bioaccumulation in the tissues and potential toxicity as carcinogens and teratogens [1]. CAHs are released together with other unintentionally persistent organic pollutants (UPOPs) from thermal process like incinerators and metal industries [2]. Therefore, it is important to develop convenient, practical and cost effective methods to remove atmospheric CAHs. Among various available techniques, catalytic combustion has been proven to be a promising and emerging technology for the removal of CAHs in waste gases, due to its highly effective character (between 250 and 550 °C) and low use of energy (without additional fuel) when compared to a thermal process [3].

Of the studies of the catalysts used in the catalytic combustion of CAHs, most have been reported on the three types of catalysts based on noble metals [4–6], transition metals [7–11] and zeolites [5,12]. Among all these catalysts, ceria-based catalyst has attracted much attention due to its remarkable redox properties and oxygen storage capability (OSC). In our previous works [13–17], one kind of ceria-based catalyst, i.e. MnO₂–CeO₂ catalyst was found to be a very active catalyst for CAHs catalytic combustion. However, it is notable that most studies on ceria-based catalysts were carried on ceria nanoparticles of polycrystal. Numerous

theoretical simulations have indicated that different crystal planes of ceria would drastically affect the catalytic property and performance, such as surface stability [18,19], oxygen vacancies formation energy [20,21], and interaction with surface molecules [22] and metals like Pt [23] and Pd [24]. Through the morphology control of the CeO₂ particle, the concept of morphology-dependent nanocatalysis not only enables the fundamental understanding of the structure–reactivity relationship, but also highlights essential implications for the design and preparation of more efficient CeO₂ and CeO₂-based catalysts. Therefore, recent studies in CeO₂ systems have focused on the structure and crystal/shape-dependent properties. For example, Li et al. have obtained single-crystalline CeO₂ nanorods ({110} and {100}) for CO oxidation, and have found that CeO₂ nanorods are more reactive than other counterparts [25]. Yan et al and Xing et al. have synthesized single-crystalline CeO₂ nanocubes ({100}) and CeO₂ nano-octahedra ({111}) by hydrothermal treatment respectively [26,27]. Overbury et al. have studied CeO₂ nano-crystals with well-defined surface planes for CO oxidation and the activity follows rods > cubes > octahedra, which can be ascribed to different mobility of lattice oxygen [28]. Dai et al. have investigated catalytic oxidation of DCE and EA over ceria exposed well-defined crystal planes, and CeO₂ nanorods turned out to be more preferable than the other two, for its higher OSC and higher mobility of oxygen [29]. Murciano has studied ceria with different morphology for oxidation of naphthalene. It was found that nanorods were more reactive than the other two, giving higher oxygen storage capacity and consequently a higher oxidation catalytic activity [30]. Moreover, the shape of CeO₂ nanoparticles has

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also been reported to strongly affect the metal–CeO₂ interaction and thus tuned up the catalytic performance of CeO₂-supported metal catalysts like Au [31], Ag [32] and Cu [33].

Our recent studies on the combustion of chlorobenzene (CB) showed that Ru/CeO₂ catalyst possesses highly stable activity for a long time [34]. The reaction mechanism involved in that C–Cl bond in CB could be dissociated easily on Ce³⁺/Ce⁴⁺ active sites and the dissociated CB could be rapidly oxidized into CO₂ and H₂O by surface reactive oxygen or lattice oxygen. The chlorine species adsorbed on the active sites could be removed in the form of Cl₂ via the Deacon reaction catalyzed by RuO₂ or CeO₂ [35]. However, there is no available information about Ru/CeO₂ catalyst in the literature related to the shape/crystal plane effect of nanoscale CeO₂ on the chemical state, structure and the reactivity of Ru species. Therefore, for better understanding of the metal–support interactions between Ru and CeO₂, the correlation of the activity of Ru/CeO₂ catalyst for CB oxidation with the shape and crystal plane of nanoscale ceria was investigated.

In this paper, we employed CeO₂-*r*, CeO₂-*c* and CeO₂-*o* as supports to prepare Ru/CeO₂ catalysts. The concentration and structure of oxygen vacancies and Ru–O–Ce in Ru/CeO₂ catalysts were investigated by means of microstrain and Raman spectroscopy, and correlated with the Ru–CeO₂ interaction. Combining with X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), diffuse reflectance UV/vis spectroscopy, X-ray photoelectron spectroscopy (XPS), hydrogen temperature-programmed reduction (H₂-TPR) and oxygen temperature-programmed desorption (O₂-TPD), we found that the shape-dependent of Ru/CeO₂ catalyst for CB oxidation were related to different status of Ru, oxygen mobility caused by oxygen vacancies, Ru–O–Ce bond and redox ability.

2. Experimental

2.1. Catalysts preparation

2.1.1. Preparation of CeO₂ with well-defined facets

CeO₂-*r*, CeO₂-*c* and CeO₂-*o* were prepared by a hydrothermal process as described in Refs. [25–27]. To obtain CeO₂-*r* and CeO₂-*c*, 3 g of Ce(NO₃)₃·6H₂O and 35.4 g (9.2 g for CeO₂-*c*) of NaOH were dissolved in 80 mL of deionized water, respectively. Then, these two solutions were mixed and kept stirring for 30 min with the formation of milky slurry. Subsequently, the mixed solution was transferred into a Teflon-lined stainless steel autoclave and then heated at 100 and 180 °C for 48 and 24 h to get CeO₂-*r* and CeO₂-*c*, respectively. After hydrothermal treatment, the precipitates were washed with distilled water and ethanol, then dried at 60 °C for 12 h and calcined in air (increasing from room temperature to 350 °C at the rate of 1 °C/min and then maintaining at 350 °C for 3 h). For CeO₂-*o*, 0.87 g of Ce(NO₃)₃·6H₂O and 0.0076 g of Na₃PO₄ were dissolved in 80 mL of distilled water. After being stirred at room temperature for 0.5 h, the mixed solution was transferred into a Teflon-lined stainless steel autoclave and heated at 170 °C for 10 h. After being cooled to room temperature, the precipitates were washed with distilled water and ethanol, then dried at 60 °C for 12 h and calcined in air (increasing from room temperature to 350 °C at the rate of 1 °C/min and then maintaining at 350 °C for 3 h).

2.1.2. Preparation of Ru/CeO₂

All three Ru/CeO₂ catalysts were prepared using the wet impregnation method. Typically, 0.5 g CeO₂ nanocrystal was slurred in deionized water under stirring, and the desired amount of 0.198 M (0.02 g_{Ru} mL⁻¹) RuCl₃ aqueous solution was added dropwise. After the impregnation, the sample was dried in a vacuum oven at RT

and then calcined in air at 400 °C for 4 h (increases from room temperature to 400 °C at the rate of 1 °C min⁻¹ and maintains for 4 h at 400 °C). The loading of Ru was calculated of 0.4% (weight ratio) for Ru/CeO₂ catalysts.

2.2. Catalysts characterization

The powder XRD of samples were recorded on a Rigaku D/Max-rC powder diffractometer using Cu K α radiation (40 kV and 100 mA). The microstrain (ϵ) of these samples were determined from line-broadening measurements on the different crystal planes, using the equation $\epsilon = \beta/4\tan\theta$. The nitrogen adsorption and desorption isotherms were measured at 77 K on an ASAP 2400 system in static measurement mode. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) model. Ruthenium content was determined by X-ray fluorescence (XRF) using a Shimadzu (XRF-1800) wavelength dispersive X-ray fluorescence spectrometer. The Raman spectra were obtained on a Renishaw in Viat + Reflex spectrometer equipped with a CCD detector at ambient temperature and moisture-free conditions. The emission line at 514.5 nm from an Ar⁺ ion laser (Spectra Physics) was focused, analyzing spot about 1 mm, on the sample under the microscope. The power of the incident beam on the sample was 3 mW. Time of acquisition was varied according to the intensity of the Raman scattering. The wave numbers obtained from spectra were accurate to within 2 cm⁻¹. UV-Vis diffuse reflectance spectra (DRS) were recorded in the range of 200–900 nm by using a Varian Cary-500 spectrophotometer. XPS measurements were made on a VG ESCALAB MK II spectrometer by using Mg K α (1253.6 eV) radiation as the excitation source. HRTEM images were taken on a JEM-2100F field emission transmission electron microscope that operated at 200 kV. Scanning electron microscope (SEM) images were recorded on a Hitachi-S4800 equipped with FEG (cold) in SE mode.

H₂-TPR of samples placed at the bottom of the U-shaped quartz tube was investigated. Prior to the H₂-TPR test, the sample (100 mg) was pre-treated with Ar flow (30 mL/min) at 400 °C for 3 h. The test was performed by heating the samples (100 mg) in H₂ (5 vol.%) / Ar flow (30 mL/min) at a heating rate of 10 °C/min from 50 to 600 °C. The hydrogen consumption was monitored by thermoconductivity detector (TCD), and the extent of reduction was quantitatively calculated according to the TPR peak areas and the result was calibrated on the basis of the hydrogen consumption from the reduction of CuO to Cu. O₂-TPD was carried out in a U-shaped quartz tube and the desorption signal of oxygen was recorded with an online mass spectrometer apparatus (HIDEN QIC-20). Prior to O₂-TPD test, the sample (100 mg) was pre-treated in a purified oxygen stream at 400 °C for 60 min, cooled down to room temperature in oxygen atmosphere and purged by a stream of purified He until stabilization of MS base line. The reactor was heated at the rate of 10 °C/min from 50 to 700 °C. Simultaneously, the desorbed oxygen signal was collected by MS detector.

2.3. Catalytic activity measurements

Catalytic combustion reactions were carried out in a continuous flow micro-reactor constituted of a quartz tube of 4 mm of inner diameter at atmospheric pressure. 200 mg catalyst as the reaction bed was packed. The feed flow through the reactor was set at 100 cm³ min⁻¹ and the gas hourly space velocity (GHSV) was maintained at 30,000 h⁻¹. Feed stream to the reactor was prepared by delivering liquid CB with a syringe pump into dry air and the injection point was electrically heated to ensure complete evaporation of the liquid reaction feeds. The concentration of CB in the reaction feeds was set at 1000 ppm. The temperature of the reactor was measured with a thermocouple located just at the bottom of the micro-reactor and the effluent gases were analyzed by an

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