Novel nanowire self-assembled hierarchical CeO$_2$ microspheres for low temperature toluene catalytic combustion
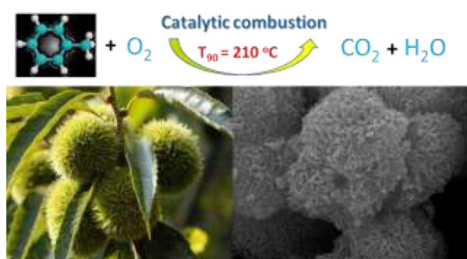
Fangyun Hu[a], Jianjun Chen[a,*], Yue Peng[a], Hua Song[a], Kezhi Li[a], Junhua Li[a,b,*]

[a] *School of Environment, Tsinghua University, Beijing 100084, China*
[b] *State Key Joint Laboratory of Environment Simulation and Pollution Control, Beijing 10084, China*

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

The catalytic oxidation of toluene has been investigated over pure CeO$_2$ hierarchical catalyst for the first time. The novel CeO$_2$ catalyst was prepared by a hydrothermal-driven assembly method. The structure of CeO$_2$ catalyst was consisted of nanowire self-assembled hierarchical microspheres. The new hierarchical CeO$_2$ catalyst showed much better catalytic activity than analogous nonporous catalyst by traditional hydrothermal method. The hierarchical CeO$_2$ catalyst could reach more than 90% toluene conversion even as low as 210 °C (T$_{90}$) under a high space velocity of 60,000 mL/(g·h). The high catalytic activities could be attributed to the large surface areas, in addition, the hierarchical porous structures provide more contents of surface oxygen vacancies for the dissociation of gaseous O$_2$ on the surface.

1. Introduction

Benzene, toluene, xylenes (BTX) kinds of volatile organic compounds (VOCs) are widespread used as solvents, gasoline additives, and chemical raw materials, hence can pose a direct risk to both the environment and human health [1,2]. Catalytic combustion of BTX into CO$_2$ and water appears very promising in this field, considering the technology features both economically available and practically effective [3,4]. Supported noble metal catalysts are extensively studied during the past decades, they exhibit better activity than the metal oxide catalysts [5,6]. However, due to noble metal catalysts are always more expensive, it is highly desirable to prepare noble-metal-free catalysts with high activity and low cost.

Engineering the shape of heterogeneous catalysts at nanoscale indeed alter their performances. Since the successful application of CeO$_2$ in the catalytic converters for automotive emission control, it has been attracted enormous interest to produce ceria nanocrystals over the past few decades [7–9]. This is particularly true with ceria catalysts, where the precise control of surface atomic arrangements can modify the reactivity of Ce^{4+}/Ce^{3+} ions, changing the oxygen release/uptake behavior of ceria, which, in turn, affects the catalytic performance [7]. The synthetic strategies include precipitation, sol–gel synthesis, surfactant–assisted synthesis, hydrothermal or solvothermal synthesis, flame spray pyrolysis, microemulsion synthesis, templates etc. [8]. By

---

* Corresponding authors at: School of Environment, Tsinghua University, Beijing 100084, China (J. Li).
  E-mail addresses: chenjianjun@tsinghua.edu.cn (J. Chen), lijunhua@tsinghua.edu.cn (J. Li).

virtue of the above methods, various shapes of ceria nanostructures including rods, cubes, wires, sheets, tubes, plates, disks, nanospheres and hollowspheres were successfully prepared which has facilitated the exploring of the morphology dependent catalytic properties on these well-defined ceria nanocatalysts [9].

Recently, there is a widespread interest in the development of hierarchically catalysts, they are often superior to their corresponding bulk materials due to their enhanced multiple functionalities [10–12]. A series of synthesis methods have been applied to the preparation of hierarchically CeO_2 architectures [13]. Lu et al. reported the hierarchical mesoporous CeO_2 microspheres with flowerlike three-dimensional (3D) structure via different hydrothermal systems, which exhibited much higher catalytic activity than the general CeO_2 in trichloroethylene combustion [14]. Through the solution-based crystallographic-oriented epitaxial growth, crystal facet-based hierarchical CeO_2 junction consisting of different facets were fabricated, on which the photocatalytic reduction of CO_2 into methane was greatly improved [15]. Li et al. synthesized a crystalline uniform hierarchically CeO_2 catalyst with tunable porosity via colloidal solution combustion synthesis, which showed excellent catalytic activity for soot and CO oxidation [16]. These investigations indicate that the hierarchically CeO_2 can provide some advantages for some new physi-chemical properties, such as high surface areas, tunable surface facets, and surface defects, etc. Thus, it is important to design functional ceria materials with certain morphology by controllable routes. To the best of our knowledge, the effect of hierarchical structure on CeO_2 catalysts in the toluene catalytic combustion behavior has not been reported in detail.

Herein, the CeO_2 with hierarchical architectures were synthesized by a facile wet chemical approach—a hydrothermal-driven assembly method—to realize controllable structures of CeO_2 microspheres. Compared with the bulk ceria, the nanowire self-assembled hierarchical ceria exhibits excellent activity in toluene combustion at low temperature. The as-prepared CeO_2 was further characterized using various techniques, to correlate the excellent catalytic performance with the surface structure.

2. Experimental

2.1. Catalyst preparation

All the reagents were used without further purification. The nano-wire self-assembled hierarchical microspheres of CeO_2 catalysts (CeO_2-HS) were synthesized by a polymer modified hydrothermal method. Ce$(NO_3)_3$·$6H_2O$ (5 mmol), 60 mmol of urea and 1 g K30 (Polyvinylpyrrolidone, $(C_6H_9NO)_n$, M = 30 000) were dissolved with 80 mL of deionized water to get a clear homogeneous solution. The resulting solution was then transferred into a Teflon-lined stainless steel autoclave. The autoclave was maintained in an oven at 100 °C for 10 h. After cooling to the room temperature naturally, the samples were centrifuged, and washed with water and ethanol for several times. The resultant solid was dried at 80 °C overnight, and then calcined at 500 °C (1 °C·min^{-1} rate) for 3 h. The microsphere CeO_2 catalysts (CeO_2-S) were obtained in a similar procedure without the addition of K30.

2.2. Catalyst characterization

N_2 adsorption–desorption isotherms were measured using Quantachrome Autosorb-1MP at liquid nitrogen temperature (77 K). XRD patterns were recorded on a Rigaku X-ray diffractometer (D/max-2200) fitted with a Cu Kα source (λ = 0.15405 nm, 40 kV and 200 mA). TG-DTG was curried on a Mettler Toledo TGA/DSC 1 STARe in air with a heating rate of 10 K/min. The Raman spectra was recorded under ambient conditions by Renishaw confocal Raman spectrometer (RM2000) using a 532 nm laser. SEM images were performed on a HITACHI SU-8010 electron microscope, operating at 30 kV. TEM images were obtained using a JEOL JEM-2100F microscope, operating

at 200 kV. The X-ray photoelectron spectroscopy (XPS) measurements were performed on a multifunctional imaging electron spectrometer (VG, ESCALAB 250XI, Thermo Scientific, Surrey) with Al Ka (hν = 1486.6 eV) radiation. H_2-TPR analysis was operated in a U-shaped quartz reactor under a gas flow with a Micromeritics Autochem 2720. The sample with 100 mg was pre-treated in Ar at 300 °C for 1 h before measurement. The samples were measured continuously by a thermal conductivity detector (TCD) from 50 to 950 °C with 10 °C/min under 10% H_2/Ar flow. The gas flow rate was 50 mL/min.

2.3. Catalyst evaluation

Toluene is a typically kind of VOCs, plays important roles in the atmosphere and directs toxicity to humans [17]. In this study, toluene combustions were carried out in a continuous flow quartz tube (Φ = 10.0 mm) micro-reactor with 100 mg catalyst (40–60 mesh) at atmospheric pressure. The volumetric composition of the reactant mixture was 1000 ppm toluene + 20% O_2 + balance N_2, and the total flow was 100 ml/min. Toluene was generated and injected using a bubbler. At the beginning of each test, the catalyst was pretreated in the real reactant mixture for 2 h in order to overcome the over-estimation of toluene catalytic combustion conversion caused by adsorption of toluene. The performances at steady states (typically after 0.5 h) were used for discussion. The concentrations of the reactants and products were monitored on line by a gas chromatograph (Agilent 7890A) by double flame ionization detectors (FID), where the CO_2 were converted into CH_4 with a methanizer nickel reactor. All results showed there were only CO_2 in the downstream gas products, indicating the toluene molecules were completely decomposed over these catalysts. In the case of water vapor addition, 5 vol% of H_2O was introduced via a mass flow controller using a water saturator.

The toluene conversion (X, %) is calculated according to the following formula:

$$X = \frac{[CO_2]_{OUT}}{7*[Toluene]_{IN}} *100\% \tag{1}$$

The normalized initial reaction rate (r, mol·m^{-2}·s^{-1}) is calculated as below:

$$r = -\frac{F}{m_{cat}*S_{BET}}*\frac{P}{RT}*\ln(1-X)*[Toluene]_{IN} \tag{2}$$

The turnover frequencies (TOF, s^{-1}) are calculated based on the following equation:

$$TOF_{OV} = \frac{X*[Toluene]_{IN}*F}{\frac{m_{cat}}{M_{CeO_2}}*(A_{600}/A_{455})} \tag{3}$$

The activation energies are calculated for toluene conversions lower than 20%, and estimate using the following Arrhenius relationship:

$$lnr = -\frac{E_a}{RT} + lnA \tag{4}$$

where F is the toluene flow rate in unit of mol s^{-1}; m_{Cat} is the catalyst amount; M_{CeO_2} is the molecular mass; TOF_{OV} is the turnover frequency based on oxygen vacancy concentration, the integral peak areas of Raman at 600 and 455 cm^{-1} (A_{600}/A_{455}) are used to quantify the concentration of oxygen vacancy. E_a is the apparent activation energy (kJ·mol^{-1}).

3. Results and discussion

3.1. Structural and morphology studies of catalysts

As the polymer K30 was used during the preparation of the CeO_2-HS catalysts, the TG analysis was performed to examine whether K30 play a role in the formation of hierarchical microspheres or not. Fig. 1 shows the TG/DTG profiles of the two precursors on the dried catalysts before