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Catalytic combustion of toluene with $La_{0.8}Ce_{0.2}MnO_3$ supported on CeO_2 with different morphologies

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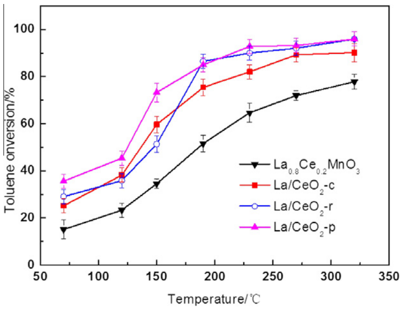
HIGHLIGHTS

- $La_{0.8}Ce_{0.2}MnO_3$ was deposited on CeO_2 with different morphologies (rod, cube and polyhedron).
- $La_{0.8}Ce_{0.2}MnO_3/CeO_2$-p exhibited the best activity during the catalytic combustion of toluene with the ignition temperature and complete conversion temperature at 128 and 240 °C, respectively.
- The higher catalytic activity of $La_{0.8}Ce_{0.2}MnO_3/CeO_2$-p was attributed to high specific surface area, small grains, more oxygen vacancies, and highly reactive oxygen species.

GRAPHICAL ABSTRACT



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ABSTRACT

Different morphologies of nano-CeO_2 (rod, cube, and polyhedron) were successfully prepared by the hydrothermal method. $La_{0.8}Ce_{0.2}MnO_3$ catalysts were deposited on the surface of these CeO_2 to obtain $La_{0.8}Ce_{0.2}MnO_3/CeO_2$ catalysts. The catalytic activity of these materials was tested for toluene catalytic combustion, and the role of nano-CeO_2 morphology on the catalyst activity was investigated. It was found that the morphology of CeO_2 had a great effect on the activity of $La_{0.8}Ce_{0.2}MnO_3$. $La_{0.8}Ce_{0.2}MnO_3/CeO_2$ nanopolyhedra exhibited the best activity at both low-temperature and high-temperature; the ignition temperature and complete conversion temperature were 128 and 240 °C, respectively. The relationship between the structural properties of different morphologies CeO_2 and the catalyst activity was investigated by scanning electron microscopy (SEM), X-ray diffraction analysis (XRD), Brunauer–Emmett–Teller (BET) and H_2-temperature programmed reduction (H_2-TPR). The higher catalytic activity of $La_{0.8}Ce_{0.2}MnO_3/CeO_2$ nanopolyhedra was attributed to high specific surface area, small grains, more oxygen vacancies, and highly reactive oxygen species. $La_{0.8}Ce_{0.2}MnO_3/CeO_2$ nanorods had poor low-temperature activity because of high reduction temperature; $La_{0.8}Ce_{0.2}MnO_3/CeO_2$ nanocubes had higher hydrogen consumption, but the smaller specific surface area limited the catalytic activity.

1. Introduction

VOCs are air pollutants that are mainly generated from industrial processes, automobile exhaust emissions, and daily human activities [1]. Most of VOCs are harmful and toxic toward

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the environment and human health because of their toxicity, carcinogenicity, mutagenicity and teratogenicity [1,2]. In order to efficiently remove VOCs, various technologies are developed, mainly including adsorption, bio-degradation, membrane separation, thermal incineration, and catalytic combustion [2,3]. Among various available processes, catalytic combustion is an effective and widely applied technology for the abatement of VOCs because it could be applied at relatively lower temperature for the thermal combustion of VOCs without the need for additional fuel [4]. The catalysts most commonly used in the combustion of VOCs are noble metals and transition metal oxides [2–5]. Although noble metals present higher activity at relatively lower temperature than transition metal oxides, their lower thermal stability, higher cost, and tendency to be poisoned limit their industrialization. Thus, more and more researchers are focusing on the design and preparation of new-type transition metal oxides as a substitute to noble metal catalysts. Some studies have proved that perovskite metal oxides catalysts (the general formula ABO_3) are excellent oxidation catalysts because of their higher thermal stability and oxygen mobility than noble metal catalysts [6,7]. But powder perovskites have low specific surface areas, which limit the catalytic activity of oxidation reaction. In order to improve their catalytic activity, perovskites are often supported on Al_2O_3, CeO_2, zeolites, cordierite, and other supports during the catalytic process [6,8]. Besides maximizing the specific surface area of the perovskite, the supports may participate in the catalytic reaction, and thus can influence the catalytic activity of the active component. Therefore, the role of the support on the catalytic combustion activity of supported-perovskites should be investigated deeply. Among various kinds of support materials, cerium dioxide is one of the most popular supports because of its chemical stability and high oxygen storage capacity due to its rich oxygen vacancy property [9,10].

Recently, remarkable progress has been made in the investigation of the morphology-dependent properties of cerium dioxide supports [9,10]. Many experimental research studies proved that different CeO_2 crystal planes exhibit different properties, for example stability [11], oxygen vacancy formation [12], and ability to react with surface molecules [13]. Rui et al. [14] have prepared Au/CeO_2 on different facets of ceria nanorods {110+100}, nanocubes {100}, and nanopolyhedra {111+100}; they found that the rodlike ceria was the most active for Au activation during the water–gas shift (WGS) reaction. A similar conclusion was also drawn by Jia et al. [15]. Although there were some works on the synthesis and catalytic activity of different morphology CeO_2 nanocrystals, there is also lack of systematic research studies on the effect of different CeO_2 morphologies on the catalytic activity of supported-perovskites for the combustion of VOCs. In the work presented in this paper, we firstly prepared $La_{0.8}Ce_{0.2}MnO_3$ perovskite catalysts supported on CeO_2 with different morphologies and then evaluated their catalytic performance in the catalytic combustion of toluene as a model VOCs. Several catalyst characterization techniques including XRD, SEM, BET, and H_2-TPR were applied to analyze the role of CeO_2 support on the performance of the supported perovskite oxide catalysts.

2. Experimental

2.1. Catalysts preparation

2.1.1. Supports preparation

CeO_2 nanopolyhedra and nanorods were synthesized via a method as reported [16]: 6 g of $C_6H_5Na_3O_7{\cdot}2H_2O$ and 2.6 g of urea were dissolved in 70 ml of deionized water; and 1.7 g of $Ce(NO_3)_3{\cdot}6H_2O$ were dissolved in 10 ml of deionized water. The two solutions were then mixed and formed an aqueous solution. After stirred for 30 min, the solution was sealed and heated at 120 °C. Heating for 24 h resulted in CeO_2 nanorods (CeO_2-r) while heating for 6 h yielded CeO_2 nanopolyhedra (CeO_2-p). When the water in the autoclave was cooled, the samples were washed, dried, and calcined for 4 h at 600 °C to obtain the final materials.

For the synthesis of CeO_2 nanocubes (CeO_2-c), the following procedure was followed: 13.9 g of $Ce(NO_3)_3{\cdot}6H_2O$ were added to a beaker containing 10 mL of deionized water while 22.4 g of NaOH were added to a beaker containing 70 mL of deionized water. Then both of the solutions were mixed and stirred magnetically for 10 min. The mixed solution was placed in a 100 mL Teflon hydrothermal reaction kettle heated at 160 °C for 24 h. Then the autoclave was cooled to room temperature. The samples were filtered, washed, and dried at 120 °C overnight. The obtained material was subsequently calcined at 600 °C for 4 h to yield CeO_2 nanocubes.

2.1.2. Supported catalyst preparation

Perovskite-type $La_{0.8}Ce_{0.2}MnO_3/CeO_2$ catalysts were prepared using the impregnation method. Different morphologies CeO_2 were used as supports, ground to a 40–60 mesh sieve after calcination at 600 °C for 4 h. $La(NO_3)_3$, $Ce(NO_3)_2$ and $Mn(NO_3)_3$, in calculated amounts (molar ratio of La:Ce:Mn = 0.8:0.2:1) and specific amount of deionized water were mixed thoroughly. The mixture was added to the amount of the CeO_2 supports and impregnated for 12 h at room temperature. Then the materials were dried in an oven at 80 °C for 12 h, and were calcined at 600 °C for 4 h. The $La_{0.8}Ce_{0.2}MnO_3/CeO_2$ catalysts were abbreviated as La/CeO_2.

2.2. Catalysts characterization

A Hitachi S-4800 scanning electron microscope (SEM) was used to obtain scanning electron micrographs. The instrument was operated using an accelerating voltage of 20 kV. The crystal phases of the catalysts were characterized by X-ray diffraction (XRD) using an X'pert Pro rotatory Diffractometer (PANalytical Co.) operated at 50 mA and 40 kV using Co Kα as radiation source (λ = 0.1790 nm). The data of 2θ from 20° to 80° were collected with a scan rate of $4^{\circ}{\cdot}min^{-1}$. Specific surface area and pore size distribution were measured by nitrogen adsorption/desorption using a Micromeritics ASAP-2010 instrument. H_2-temperature programmed reduction (H_2-TPR) tests were conducted on CHEMBET-300 (Cornell Co.) by heating the catalyst in H_2 (10 vol%)/Ar flow ($30\ ml{\cdot}min^{-1}$) at a heating rate of $10\ ^{\circ}C{\cdot}min^{-1}$ from 50 to 800 °C. The hydrogen consumption was detected by thermal-conductivity detector (TCD). Before analysis, the samples were loaded into the reactor and purged with helium ($30\ ml{\cdot}min^{-1}$) at 300 °C for 1 h to eliminate contaminants, and then cooled down to room temperature.

2.3. Catalyst evaluation

The catalytic combustion reaction was investigated with the catalysts used in a continuous flow fixed-bed stainless steel tube reactor (i.d. = 20 mm, length = 550 mm). The catalyst (3 ml, 40–60 mesh) was mixed with an equal amount of quartz sand (40–60 mesh) and was fixed in the middle of the reactor by quartz fiber. The pollutant inlet was $300\ mg{\cdot}m^{-3}$ toluene and the gas hourly space velocity (GHSV) was $12{,}000\ h^{-1}$. The inlet and outlet gases were analyzed by VARIAN CP-3800 equipped with a FID.

3. Results and discussion

3.1. Catalytic behavior for toluene oxidation

The catalytic activities of the different morphologies La/CeO_2 for toluene oxidation were tested and results are presented in Fig. 1. In