



Synthesis of three-dimensionally ordered macroporous Al–Ce mixed oxide catalysts with high catalytic activity and stability for diesel soot combustion



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ABSTRACT

A series of three-dimensionally ordered macroporous (3DOM) Al–Ce mixed oxide catalysts were prepared by the colloidal crystal templating method. The obtained catalysts were characterized by means of XRD, SEM, BET, H₂-TPR, and Raman spectroscopy. The effects of an Al/Ce ratio on the phase structure and catalytic performances were investigated. Al–Ce mixed oxide catalysts could form solid solutions with moderate aluminum content. 3DOM samples showed higher catalytic activity for soot combustion than corresponding disordered macroporous (DM) ones due to enhanced contact efficiency between the soot and the catalyst. 3DOM mixed oxide catalyst with aluminum to cerium ratio of 3:7 shows the highest catalytic activity for soot combustion, in which the values of T_{10} , T_{50} , and T_{90} are 297, 384, and 427 °C, respectively. The doping of Al into CeO₂ catalysts can enhance the catalytic stability of the catalyst. After 6-cycle runs, the T_{50} value of 3DOM samples with alumina:cerium (3:7) and alumina:cerium (6:4) have no significant change. Furthermore, the effect of thermal treatments on the catalytic properties for soot combustion was also studied. Compared with 3DOM bare CeO₂, 3DOM Al–Ce mixed oxide catalysts exhibited higher thermal stability because aluminum can prevent cerium particles from agglomeration.

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1. Introduction

Soot particulate matter (PM) emitted from diesel exhaust is hazardous to human health and global environment [1,2]. The size of the soot is so small that it can penetrate deeply into the breathing tract and deposit in the lung region, and then causes potential mutagenic and carcinogenic activity [3]. Thus, it is crucial to reduce emissions of PM before the wide utilization. The combination of traps and oxidation catalysts in the continuously regenerating particulate trap (CRT) appears to be one of the most efficient and economic after-treatment techniques for diesel engines. This key challenge is to find effective catalysts for soot combustion that operates at low temperature [4]. Many kinds of catalysts, including transition metal oxide [5], precious metal [6–8], alkaline metal oxides [9], perovskite or perovskite-like oxides [10–13], and spinel-type oxides [14], rare earth metal oxides [15], hydroxalite mixed oxides [16–18], have been investigated for soot combustion.

Among the reported catalysts, cerium oxide with the advantages of the high oxygen storage capacity, d-electron orbital, good sulfur-resistance, and excellent redox properties have gained much attention for the utilization in diesel soot oxidation [19]. However, CeO₂ alone as a catalyst or as a support in passive regeneration of particulate filter is probably of little interest because of its low textural stability for high-temperature reactions, usually encountered in the exhaust gases [20]. When CeO₂ was exposed to the high temperatures, its surface area decreases drastically and at the same time it could lose its redox properties and oxygen storage ability to a large extent. It is well known that doped ceria with proper cations has different benefits on the catalytic features of this material, improving the thermal stability, surface reducibility, oxygen storage capacity, and oxygen mobility within the framework [21]. Therefore, many attempts have been made to the doping of ceria with various ions, such as Zr, La, Ga, and K [15,22]. In addition, the loading of CeO₂ on a thermally stable, high-surface area support, such as Al₂O₃ and SiO₂, has been found to exhibit higher thermal stability [23,24]. Recently, Al composition was introduced into ceria–zirconia solid solution as a “diffusion barrier”, so that the increasing sizes of CeO₂ particles are restricted. It has been proved that a mixture of nanometer-sized CeO₂ and γ -Al₂O₃ possesses higher oxygen storage capacity than pure CeO₂ [25]. Based on the

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above considerations, a series of ceria–alumina mixed oxides have the potential as a catalyst with high stability for soot combustion.

Many investigations have shown that the contact condition between the soot and the catalyst, and the intrinsic activity of the catalyst are main influencing factors for soot combustion [26]. The contact between the catalyst and soot particles is very important for soot combustion reaction, which is a complicated solid–solid–gas reaction [6]. The conventional catalysts have smaller pore sizes (<10 nm) than soot particles (>20 nm) [8]. Therefore, soot particles cannot enter the inner pores of catalysts, which limit the process of catalyzing soot combustion and restrict available active site amounts. In this work, a series of three-dimensionally ordered macroporous (3DOM) Al–Ce mixed oxide materials were prepared by the colloidal crystal template (CCT) method. The crystal structures, redox behaviors, the effects of aging temperature, and durability of 3DOM Al–Ce mixed oxide catalysts were systematically studied. Moreover, the relationships among molar ratio of Al/Ce in the starting material, the surface area, the ordering of macropores and catalytic activities were also investigated. The pores (>50 nm) of these catalysts are big enough to permit diesel soot particles to enter their inner pores where the soot catalytic combustion reaction can proceed [8,15]. 3DOM Al–Ce mixed oxide catalysts shows high catalytic activity and stability for soot combustion. It indicates that an Al dopant plays an important role in the catalytic and thermal stability of Al–Ce mixed oxide catalysts.

2. Experimental

2.1. Catalysts preparation

2.1.1. Preparation of monodispersed PMMA colloidal spheres

Monodispersed polymethyl methacrylate (PMMA) microspheres were prepared by the surfactant-free emulsion polymerization technique and were packed into colloidal crystal templates by centrifugation according to the previous report [27]. The typical procedures for the preparation are as follows. Before preparation, the methyl methacrylate (MMA) monomer was washed with NaOH solution and distilled water four times in a separatory funnel. The washed MMA was followed with vacuum distillation. Potassium persulfate (KPS) with a small amount of water was dissolved in 40 °C water bath. The thermal solution was filtered rapidly, and the filtrate was cooled to crystallization by ice water. The crystal was filtered and washed by ice water until no SO_4^{2-} and then dried in a vacuum oven at 40 °C. When refined materials were obtained, a certain amount of pre-treated MMA monomer and distilled water was added to a 2000 mL four neck round-bottomed flask equipped with a condenser, stirring paddle, an inlet port for argon, and another port for materials. The mixture was stirred at a speed of 350 r/min, and argon was introduced to remove the air inside the flask to afford an inert reaction atmosphere. After about half an hour, moderate pre-treated KPS solution was added to initiate polymerization, the temperature of the reaction system was raised to 80 °C. The polymerization reaction was conducted under this temperature for 2 h. After the reaction was finished, the reaction system was naturally cooled to room temperature, and filtered to obtain the homogenous latex with nearly monodispersed PMMA colloidal spheres.

2.1.2. Assembly of PMMA colloidal crystal templates

The 3DOM PMMA colloidal crystal templates were assembled via a centrifugation method [28]. A certain amount of PMMA latex was centrifuged at a rate of 3000 rpm for 10 h. After the PMMA colloidal spheres were fully precipitated, the supernatant was carefully removed by a dropper. The well-arranged PMMA colloidal spheres are then dried in a vacuum oven at 40 °C. Finally, the highly ordered PMMA colloidal crystal templates for synthesis of 3DOM

Al–Ce mixed oxide catalysts were obtained. The preparation of 3DOM materials is closely related to the uniform particle size and spherical morphology of PMMA microspheres.

2.1.3. Preparation of 3DOM Al–Ce mixed oxide catalysts

3DOM Al–Ce mixed oxide catalysts were prepared via a precursor thermal decomposition-assisted colloidal crystal templating method. Typically, stoichiometric amounts of citric acid were dissolved into 10 mL of ethanol (95%wt) by stirring in a 50 mL beaker at room temperature for 30 min, and then required amount of metal nitrates $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in the mixed solvent to achieve the precursor solution [29]. Dried PMMA colloidal crystal templates were permeated in the precursor solutions for 2 h by impregnation (PMMA is a kind of hydrophilic polymer) and excess precursor solutions were filtered. The filtered PMMA colloidal crystal templates were then dried overnight at 323 K. Finally, the dried PMMA colloidal crystal templates were mixed with quartz sand (10–15 mesh) and calcined in air under temperature linearly rising to 310 °C at a rate of 1 °C/min and held for 4 h to remove PMMA colloidal crystal templates, and subsequently linearly rising to 600 °C at a rate of 1 °C/min in air and kept at 600 °C for 5 h. In this process, the quartz sand played the role of heat dissipation, which could prevent the sintering of 3DOM catalysts. Finally, 3DOM catalysts were obtained by separation in the mixture of the catalyst and quartz sand. The obtained Al–Ce mixed oxides with different mole ratios are denoted as AlCe (x:y), where x:y represents the molar ratio of Al to Ce.

The preparation of 3DOM pure CeO_2 catalysts is similar to that of AlCe (x:y) catalysts. 1.05 g citric acid were dissolved into 10 mL of ethanol (95%wt) by stirring, then 2 mol $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were dissolved into the solvent. Through the immersion process, PMMA colloidal crystal templates were permeated in the precursor solutions. After 2 h, excess precursor solutions were filtered and dried overnight at 323 K. Finally, the dried PMMA were heated under the same calcination conditions as the synthesis of 3DOM AlCe (x:y) catalysts.

2.1.4. Preparation of DM Al–Ce mixed oxide catalysts

DM AlCe (3:7) and AlCe (6:4) oxide catalysts were prepared with the combination of ethylene glycol-ligation and solution combustion by using $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as starting materials [30]. The stoichiometric amounts of mixed metal nitrates were dissolved with ethylene glycol (EG) by stirring at room temperature, and the produced EG solution was poured into a volumetric flask. EG solution of the mixed metal nitrate was heated in an electric furnace from room temperature to solution combustion completely. Then EG was oxidized to the glyoxylate dianion in aqueous solution by nitrate of mixed metals at low temperatures (<100 °C). The metal glyoxylate converted to their metal oxide at relatively low temperatures (up to 400 °C). And the perfect crystal phases were obtained by further calcination at 600 °C for 5 h. The obtained catalysts have a lot of disordered macropores.

2.2. Activity tests of catalysts

The catalytic performances of all the catalysts were evaluated with a temperature-programmed oxidation reaction (TPO) on a fixed-bed tubular quartz system ($\Phi=8$ mm). The reaction temperature runs from 150 to 650 °C at a 2 °C/min rate through a PID regulation system based on measurements with a K-type thermocouple. The model soot (Printex-U) used in this work was purchased from Degussa. Its primary particles size and specific surface area is 25 nm and 100 m²/g, respectively. Elemental analysis showed its carbonaceous nature with 92.0% C, 0.7% H, 3.5% O, 0.1% N, 0.2% S, and 3.5% other [7]. In order to reproduce the loose contact mode (just physical contact by shaking the soot and the catalyst in a

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