

Preparation of ultrafine Ce-based oxide nanoparticles and their catalytic performances for diesel soot combustion

WEI Yuechang (韦岳长), ZHAO Zhen (赵震)*, JIAO Jinqing (焦金庆), LIU Jian (刘坚), DUAN Aijun (段爱军), JIANG Guiyuan (姜桂元)

(State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, China)

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Abstract: The ultrafine Ce-based oxide nanoparticles with different element dopings (Zr, Y) were synthesized by the method of micropores-diffused coprecipitation (MDC) using ammonia solution as the precipitation agent. The activities of the catalysts for soot oxidation were evaluated by the temperature-programmed oxidation (TPO) reaction. Ce-based oxides prepared in this study exhibited high catalytic activity for soot oxidation under the condition of loose contact between soot particles and catalysts, and the catalytic activity of ultrafine $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ nanoparticle for soot combustion was the highest, whose T_{10} , T_{50} and $S_{\text{CO}_2}^m$ was 364, 442 °C and 98.3%, respectively. All catalysts were systematically characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Brumauer-Emmett-Teller (BET), Fourier transform infrared spectroscopy (FT-IR) and UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS). It was indicated that the MDC method could prepare the ultrafine Ce-based oxide nanoparticles whose the crystal lattice were perfect, and the BET surface area and average crystal size of the ultrafine nanoparticles changed with the different element dopings (Zr, Y). The H_2 -TPR measurements showed that the ultrafine Ce-based oxide nanoparticles with the doping-Zr cation could be favorable for improving the redox property of the catalysts.

Keywords: ultrafine nanoparticles; Ce-based oxides; catalysts; soot combustion; micropores-diffused coprecipitation; rare earths

Particulate matter (PM, mainly containing soot particles) emitted from diesel engines has caused acute human health and environmental problems^[1]. This calls for efficient exhaust gas treatment systems for diesel engines. The continuously regenerating particulate trap (CRT) technology with the combination of oxidation catalysts and traps appears to be one of the most efficient after-treatment techniques^[2]. The key challenge is to find a catalyst with the lower oxidation temperature of soot particles. Several kinds of catalysts such as precious metal^[3,4], alkaline metal oxides^[5], perovskite or perovskite-like type oxides^[6] and ceria-based materials^[7,8] have been widely studied for diesel soot combustion. Especially, noble metal catalysts such as platinum and gold are efficient and exhibit high activity^[9,10]. However, the price of Au or Pt is very expensive. Thus, the development of active and stable catalysts without noble metals for the catalytic combustion of soot at relatively low temperature remains a significant challenge.

Ce-based oxides as important component have been widely used in the three-way catalysts to control automobile exhaust due to their oxygen storage/release capacity (OSC)^[11,12]. Some Ce atoms in CeO_2 crystal lattice are replaced by Zr or Y cations to form Ce-based solid solutions, the replacement would lead to the microstrain.

And Ce-based oxides show better OSC performance, higher thermal stability and excellent catalytic activity^[13], it is possible to meet the needs of narrow and high catalytic active temperature for diesel emission purification. The heterogeneous catalytic reaction containing solid reactant is a class of important and complex chemical reaction. To design and synthesize high performance materials in terms of catalytic activity, understanding the properties affecting catalytic performance is of great importance. The nature of catalyzing soot combustion is a kind of deep oxidation reaction which takes place at the three-phase boundary among a solid catalyst, a solid reactant (soot) and gaseous reactants (O_2 , NO)^[14]. Thus, the catalytic activity for diesel soot combustion is affected by two factors: the contact efficiency between soot particles and the catalysts, and the intrinsic activity of material^[15]. So how to effectively improve the contact efficiency between soot particles and catalysts is a key factor affecting the catalytic activity for soot combustion.

Motivated by the above considerations, the catalysts of ultrafine Ce-based oxide nanoparticles with different element dopings (Zr, Y) were synthesized by the method of micropores-diffused coprecipitation (MDC) using the ammonia solution as precipitation agent, and exhibited

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* **Corresponding author:** ZHAO Zhen (E-mail: zhenzhao@cup.edu.cn; Tel.: +86-10-89731586)

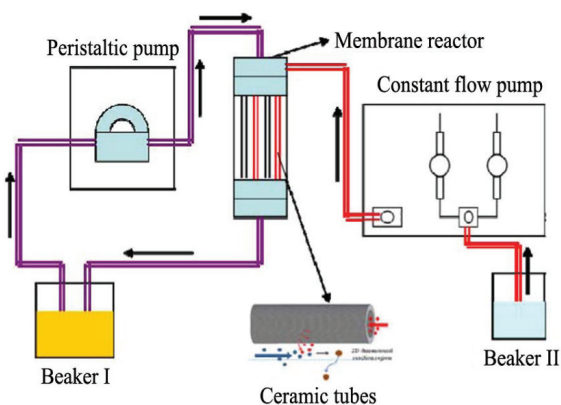
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high catalytic activity for soot combustion. It is because the ultrafine oxide nanoparticles can improve the contact efficiency between soot particles and catalysts. Therefore, the shape-controlled synthesis of the ultrafine oxide nanoparticle catalyst is a potential route for enhancing the catalytic activity for soot combustion.

1 Experimental

1.1 Catalyst preparation

The ultrafine Ce-based oxide nanoparticle catalysts with different element dopings (Zr, Y) were synthesized by micropores-diffused coprecipitation (MDC) method derived from the method of ultrasonic-assisted membrane reaction (UAMR)^[13,16]. The schematic diagram of the preparation device is shown in Scheme 1. The core of the MDC device is the ceramic membrane reactor composed of four ceramic membrane tubes on which there are abundant nanometer holes on the wall, which are used for highly homogeneous dispersion of precipitation agent. The typical synthesis process was described as follows: Stoichiometric amounts of $\text{Ce}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ and/or $\text{Zr}(\text{NO}_3)_4 \cdot 3\text{H}_2\text{O}$ or $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Shandong Yutai County Fine Chemical Factory) were mixed and stored in a precursor tank (Beaker I). The solution containing ammonia and certain amount of polyethylene glycol (PEG) was stored in another tank (Beaker II) as precipitation agent. The molar ratio of $\text{Ce}_{1-x}\text{Zr}(Y)_x\text{O}_2$, PEG and $\text{NH}_3 \cdot \text{H}_2\text{O}$ is 1:1:6. As the precursor solution (Beaker II) was diffused into the membrane reactor via the holes (40 nm) distributed on the wall of the ceramic membrane tubes by a constant flow pump, the coprecipitation of Ce^{3+} , Zr^{4+} or Y^{3+} occurred while meet precipitation agent in membrane reactor, yielding $\text{Ce}(\text{OH})_3$, $\text{Ce}(\text{OH})_3\text{-Zr}(\text{OH})_4$ or $\text{Ce}(\text{OH})_3\text{-Y}(\text{OH})_3$. The slurry mixture was deposited, filtered and dried at 80 °C, and then calcined at 550 °C for 4 h in a static air. Finally, the ultrafine Ce-based oxide nanoparticles were obtained.



Scheme 1 Schematic diagram of the micropore-diffused coprecipitation device for synthesis of ultrafine Ce-based oxide nanoparticle catalysts

1.2 Catalytic activity measurement

The catalytic activities of the catalysts were evaluated with a temperature-programmed oxidation reaction (TPO) on a fixed-bed tubular quartz reactor ($\Phi=8$ mm). The model diesel soot particles used in this work was Printex-U (diameter 25 nm, purchased from Degussa). Catalyst (0.1 g) and soot (0.01 g) were mixed at a mass ratio of 10:1 using a spatula in order to reproduce the loose contact mode. It is the most representative model of diesel particles flowing through a catalytic filter. The reaction temperature was controlled through a PID-regulation system and varied from 150 to 600 °C at a rate of 2 °C/min for each TPO run. Reactant gases containing 5 vol.% O_2 and 0.2 vol.% NO balanced with He passed through a mixture of the catalysts and soot particles at a flow rate of 50 mL/min. The outlet gas compositions were analyzed with an on-line gas chromatograph (GC, Sp-3420, Beijing) with a flame ionization detector (FID). The catalytic activity for soot combustion was evaluated by the values of T_{10} , T_{50} and T_{90} during the TPO procedure, which was defined as the temperatures at 10%, 50% and 90% of soot conversion, respectively. The selectivity to CO_2 formation (S_{CO_2}) was defined as that the CO_2 outlet concentration divided by the sum of the CO_2 and CO outlet concentrations. The $S_{\text{CO}_2}^m$ was denoted as the S_{CO_2} at the maximum temperature (T_m), at which soot burnt rate was the highest, i.e., $S_{\text{CO}_2}^m = [\text{CO}_2]_{\text{outmax}} / ([\text{CO}_2]_{\text{outmax}} + [\text{CO}]_{\text{outmax}}) \times 100\%$.

1.3 Catalyst characterization

The Brunauer-Emmett-Teller (BET) method was used to measure the specific surface areas of the catalysts. XRD patterns were measured on a powder X-ray diffractometer (Shimadzu XRD 6000) using Cu K α ($\lambda=0.15406$ nm) radiation with a Nickel filter operating at 40 kV and 10 mA in the 2θ range of 20°–80° at a scanning rate of 4 (°)/min. The patterns were compared with JCPDS reference data for phase identification. The crystallite sizes of obtained catalysts were calculated from the width of the (111) line using the Scherrer equation: $D=0.9\lambda/(\beta\cos\theta)$, where λ is the wavelength of the radiation, β is the corrected peak width at half-maximum intensity (FWHM), and 2θ is the peak position. FT-IR absorbance spectra were obtained in the wavenumber ranging between 4000 and 400 cm^{-1} via an FTS-3000 spectrophotometer manufactured by American Digilab company, the measured wafer was prepared as KBr pellet with the weight ratio of sample to KBr, 1:100. The resolution was set at 4 cm^{-1} during measurement. The UV-Vis DRS experiments were performed on a Hitachi U-4100 UV-Vis spectrophotometer with the integration sphere diffuse reflectance attachment. The powder samples were loaded in a transparent quartz cell and were measured in the region of 200–800 nm at room tempera-

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