Journal of Colloid and Interface Science 532 (2018) 579–587

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

# Roles of cobalt and cerium species in three-dimensionally ordered macroporous $Co_xCe_{1-x}O_\delta$ catalysts for the catalytic oxidation of diesel soot

Baofang Jin[a], Xiaodong Wu[a,*], Duan Weng[a], Shuang Liu[b], Tingting Yu[c], Zhen Zhao[c], Yuechang Wei[c]

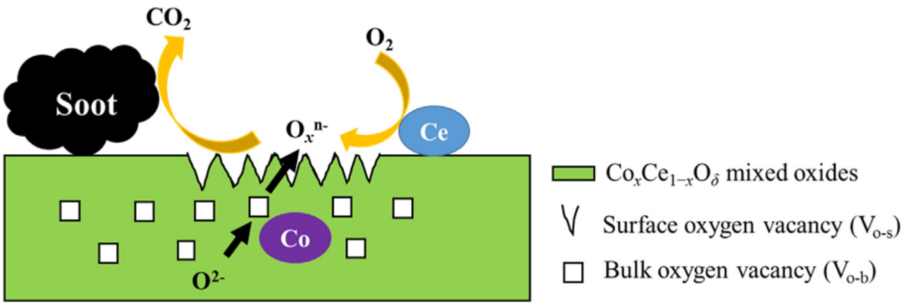
[a] The Key Laboratory of Advanced Materials of Ministry of Education, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China
[b] Institute of Materials Science and Engineering, Ocean University of China, Qingdao 266100, China
[c] State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, China

## HIGHLIGHTS

- $Co_xCe_{1-x}O_\delta$ catalyst shows higher activity than that of single $CeO_2$ and $Co_3O_4$.
- Strong interactions exist between Co and Ce cations via electron transfer.
- Ce facilitates the creation of surface oxygen vacancy ($V_{O\text{-}s}$) to ignite soot oxidation.
- Co promotes the mobility of lattice oxygen via increasing bulk oxygen vacancies ($V_{O\text{-}b}$).

## GRAPHICAL ABSTRACT

Ce facilitates the creation of surface oxygen vacancy ($V_{O\text{-}s}$) and Co promotes the mobility of lattice oxygen via increasing bulk oxygen vacancies ($V_{O\text{-}b}$).



## ARTICLE INFO

*Article history:*
Received 16 June 2018
Revised 6 August 2018
Accepted 7 August 2018
Available online 9 August 2018

*Keywords:*
$Co_xCe_{1-x}O_\delta$ mixed oxides
Soot oxidation
Electron transfer
Oxygen vacancy

## ABSTRACT

Three-dimensionally ordered macroporous (3DOM) $Co_xCe_{1-x}O_\delta$ oxides with different Co/Ce atomic ratios were synthesized by a colloidal crystal template (CCT) method. They show higher activity for soot combustion in $O_2$ than single $CeO_2$ and $Co_3O_4$ under loose contact conditions. XRD, Raman, XPS, $H_2$-TPR and soot-TPR characterizations were carried out to study the surface and bulk oxygen vacancies and to correlate them to the activity. There exists electron transfer from Ce to Co in the matrix. Both $Ce^{3+}$ and $Co^{2+}$ species contribute importantly to the creation of surface and bulk oxygen vacancies, which determine the ignition and burnout temperatures of the catalysts, respectively.

## 1. Introduction

Due to the advantages of highly efficiency, low operating costs and excellent durability, diesel engines are of great importance to modern society and have been widely used in power generation, farming, construction and industrial activities [1]. However, particulate matters (PM) emited from diesel engines seriously threaten atmospheric environment and human health [2–4]. In response to the rigorous emission standards, continuous endeavors have been taken in reducing soot emission. Currently, the combination of catalytic combustion technique and diesel particulate filters

---

* Corresponding author.
*E-mail address:* wuxiaodong@tsinghua.edu.cn (X. Wu).

https://doi.org/10.1016/j.jcis.2018.08.018
0021-9797/

(DPF) is regarded as the most promising after-treatment technology to remove PM from the exhaust streams [5]. As the major part of PM and the most difficult to burn, soot combusts naturally at around 550–600 °C in air atmosphere, while the exhaust gas temperature is generally located between 200 and 500 °C. Therefore, the key challenge is to find effective catalysts on filters, which could oxidize soot at low temperatures [6–7].

Ceria is always a constituent of three-way catalysts due to its high oxygen storage capacity, which results in alternating oxygen composition between $Ce^{3+}$ and $Ce^{4+}$ [8–9]. The insertion of metallic dopants into the lattice of ceria can produce structural defects and further improve oxygen mobility [10]. Cobalt, in particular, has been received much attention duo to its beneficial effect on ceria. Similar to ceria, cobaltosic oxide ($Co_3O_4$) also has variable chemical valence states ($Co^{3+}$ and $Co^{2+}$). The aliovalency exists in its pure oxide and even its solid solution with ceria [11]. Therefore, Ce-Co mixed oxide could improve mobility of oxygen ions and enhance the oxygen storage-release of the catalytic system, which promote the efficiency of the $Co^{3+}$–$Co^{2+}$ and $Ce^{3+}$–$Ce^{4+}$ redox couples. In addition, the synergistic effect between $Co_3O_4$ and $CeO_2$ stimulates the dispersion of the $Co_3O_4$ phase on the surface at the proper Co content. The features of Co-Ce mixed oxide catalyst can lead to superior catalytic performance in a lot of reactions, such as low temperature CO oxidation [12–14], methane oxidation [15] and $N_2O$ decomposition [16]. Lu et al. found that Co-Ce mixed oxides prepared by a sol-gel method exhibit the excellent catalytic activity for soot oxidation, which is attributed to the high NO oxidation activity and high $NO_2$ storage capacity [17]. Shangguan et al. prepared Co-Ce mixed oxides by a citric acid complex method and found that $Co_{0.93}Ce_{0.07}$ sample acquired the best catalytic activity for soot oxidation under tight contact with $T_{10} = 315$ °C and $T_{50} = 370$ °C [9].

Despite the ability to provide active oxygen for soot oxidation, these traditional powder catalysts have small pore sizes (<10 nm), which is not allowed soot particles (ca. 25 nm) to enter the inner of the catalysts. This limits the process of catalyzing soot oxidation and restricts the availability of active sites [18–20]. According to the previous report, three dimensionally ordered macroporous (3DOM) oxides with large pore sizes (>50 nm) and interconnected macroporous tunnels not only permit soot particles to touch the active sites on the internal surfaces of the catalysts, but also make soot particles to transfer easily through the open structure and have less diffusion resistance to reach active sites [21].

Motivated by the above considerations, 3DOM Co-Ce mixed oxide catalysts were prepared in this work. It was found that the strong interactions between Ce and Co played a vital role in enhancing their catalytic performances for soot oxidation in $O_2$. The influences of surface and bulk oxygen vacancies on the ignition and burnout temperatures of soot oxidation were investigated by tuning the Co/Ce molar ratio of the mixed oxides.

## 2. Experimental

### 2.1. Catalyst preparation

Monodispersed poly(methyl methacrylate) (PMMA) microspheres were synthesized by an emulsifier-free emulsion method. Before use, the spheres should be close-packed array by centrifugation to act as colloidal crystal templates. The detailed procedures were reported previously [22].

3DOM $Co_xCe_{1-x}O_\delta$ catalysts with different Co/Ce molar ratios were synthesized by a colloidal crystal template (CCT) method. Typically, the requisite quantities of citric acid, metal nitrates $Ce(NO_3)_3{\cdot}6H_2O$ and $Co(NO_3)_3{\cdot}6H_2O$ were mixed into an ethanol (95 wt%) solution by manetic stirring. Then, PMMA templates were placed in the precursor solution for 2 h. The total metal molar quantity was 0.02 mol and the mass of PMMA was 10 g. After removing the excess precursor solution by filtration, the obtained sample was dried overnight at 50 °C. Afterwards, the dried sample was mixed with commercial alumina pellets with the diameter of ca. 3 mm. The mixed sample was calcined in air from room temperature to 310 °C at a rate of 1 °C/min and held for 4 h to remove the organic templates, and subsequently to 550 °C and kept at 550 °C for 4 h. Finally, 3DOM catalysts were obtained by separation from the alumina pellets. The obtained mixed oxides were denoted as $Co_xCe_{1-x}O_\delta$, where $x$ represented the molar ratio of Co. The pure 3DOM $CeO_2$ and $Co_3O_4$ were also prepared by the same method.

### 2.2. Activity measurement

The catalytic activities of the catalysts were carried out by the soot temperature-programmed oxidation (TPO). The primary particles size and specific surface area of model soot (Printex-U, Degussa) was ca. 25 nm and 100 $m^2/g$, respectively. To evaluate the activity of the catalyst in loose contact with soot, typically, 10 mg soot was mixed with 100 mg catalyst using a spatula. Another 300 mg silica was added to prevent reaction runaway. The mixture was heated from room temperature to 650 °C at a rate of 5 °C/min. The inlet gas mixture was 10% $O_2$ /$N_2$ with a total flow rate of 500 mL/min. The productions of CO and $CO_2$ were on-line monitored by an infrared spectrometer (Nicolet iS10, Thermo Corp). The temperatures at the soot conversion of 10%, 50%, and 90% were defined as $T_{10}$, $T_{50}$ and $T_{90}$. The selectivity to $CO_2$ formation ($S_{CO2}$) was defined as $S_{CO2} = C_{CO2}/(C_{CO} + C_{CO2})$ in which $C_{CO}$ and $C_{CO2}$ were the concentration of CO and $CO_2$, respectively.

### 2.3. Catalyst characterization

The powder X-ray diffractometer (Shimadzu XRD 6000) were employed to identify the structures of catalysts operating at 40 kV and 10 mA, using Cu Kα radiation ($\lambda = 1.54184$ Å) and Ni filter. The X-ray diffracto grams were recorded with a scanning velocity of 4°/min from 5 to 90°. The patterns were compared with JCPDS reference data for phase identification. The lattice constant and crystallite size of $CeO_2$ in the catalysts was calculated by Bragg equation and Williamson-Hall formula, respectively.

The $N_2$ adsorption and desorption were carried out by Micromeritics ASAP 2020 analyzer at −196 °C. The samples were degassed in $N_2$ at 300 °C for 3 h before the experiment. The specific surface are of the samples were calculated by the BET method.

The morphologies of the samples were observed through both scanning electron microscope (SEM) on a Quanta 200F instruments. Samples were dusted on an adhesive conductive carbon belt attached to a copper disk and were coated with Au prior to measurement.

X-ray photoelectron spectra (XPS) data were recorded on a Perkin–Elmer PHI-1600 ESCA spectrometer using Mg Ka (hv = 1253.6 eV) as X-ray source. All measured binding energies were calibrated using C1s peak of contaminant carbon (BE = 284.6 eV) as an internal standard.

The laser Raman spectroscopy measurements were obtained at RT by using a LabRAM HR 800 (HORIBA Jobin Yvon, France) spectrometer. A laser radiating at 532 nm was used for exciting source from an argon ion laser, and the laser power of below 0.06 mW was applied at the sample.

Temperature-programmed reduction with $H_2$ ($H_2$-TPR) was performed on the Micromeritics Auto Chem II 2920 apparatus. 50 mg sample was placed in a U-shaped quartz tube and pretreated in a Ar stream at 300 °C for 1 h. After the samples were cooled to 30 °C, the gas was changed into 10% $H_2$/Ar flow (50 mL/min).