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Process Safety and Environmental Protection

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

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Washcoating of cordierite honeycomb with ceria-copper mixed oxides for catalytic diesel soot combustion

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ARTICLE INFO

Article history:

Received 6 March 2015

Received in revised form 21 November 2015

Accepted 1 December 2015

Available online 28 January 2016

Keywords:

Diesel soot oxidation

Mixed oxides

Ceria

Cordierite coating

Automotive catalysis

Diesel particulate filter

ABSTRACT

Cordierite honeycomb monoliths coated with ceria-copper catalyst were synthesized, characterized, and used in catalytic soot oxidation. First, $\text{Ce}_{0.6}\text{Cu}_{0.4}\text{O}_2$ was obtained by the sol-gel method and deposited on cordierite. The resulting material was employed to capture and oxidize soot. The coating process generated highly dispersed active species and enriched the coating surface with ceria and copper. XRD, H_2 -TPR, OSC, Raman spectroscopy, and SEM and TEM microscopies helped to confirm the structural and morphological properties of the material and formation of the mixed oxides. Compared with the uncatalyzed reaction, thermogravimetry analysis (TGA/DTA) of the soot oxidation in the presence of the catalysts showed that the soot oxidation temperature decreased. Raman spectroscopy studies revealed an increased number of oxygen vacancies in the $\text{Ce}_{0.6}\text{Cu}_{0.4}\text{O}_2$ deposited on cordierite as compared with pure CeO_2 deposited on cordierite. The coated monolithic catalyst exhibited desirable catalytic performance the soot removal rate exceeded 73% according to dynamic tests conducted in a stationary engine.

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1. Introduction

Diesel engines have long been used in many types of vehicles: they display high fuel efficiency and durability (Fino and Specchia, 2008). However, emissions from this or other types of engines consist mostly of nitrogen oxides (NO_x), carbon oxides (CO_x), and soot particles (Dou, 2012; Dhanushkodi et al., 2008; Hernández-Giménez et al., 2013), which affect the human health and cause respiratory diseases (Müller et al., 2006; Bünger et al., 2012; Tsai et al., 2012; Russell and Epling, 2011; Neeft et al., 1996). Awareness about the need to abate soot release by diesel engine exhausts has increased, as noted from the environmental legislation on exhaust specifications (Twigg, 2007; van Setten et al., 2001; Vouitsis et al., 2003; Simonsen et al., 2008; Cousin et al., 2007; Meynen and González-Velasco, 2014).

One strategy to diminish soot emission has been to design catalytic filters or traps that combine soot retention and combustion (Nascimento et al., 2014a; Lebukhova et al., 2015; Wei et al., 2011). This way, the filters need to be regenerated periodically in oxidizing atmosphere at higher temperatures or regenerated continuously in the presence of catalysts at low temperatures. Cordierite honeycomb is considered an excellent ceramic material to produce diesel particulate filters (DPFs) due to its high melting point, high temperature and thermal shock resistance, high surface area, high chemical stability, and good adhesion of the catalysts (Neyertz et al., 2014). Such filters may employ catalysts that promote low-temperature combustion of carbonaceous materials, to reduce the amount of diesel soot. Since these materials are oxidized over 550°C and because the exhaust gases usually cool down to $300\text{--}400^\circ\text{C}$, these catalysts should perform well at these low

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<http://dx.doi.org/10.1016/j.psep.2015.12.010>

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temperatures (Jiménez et al., 2010; Kumar et al., 2012). Catalysts can be used in a number of possibilities to accelerate combustion of the accumulated soot. Catalytic combustion of the diesel carbonaceous particulate matter relies on a heterogeneous reaction involving solid soot particles, the exhaust gases, and the solid catalyst in intimate contact with the filter and is a key parameter for efficient and fast oxidation (van Setten et al., 2001; Lebukhova et al., 2015; Wei et al., 2013). On the other hand, the catalytic activity of the solids depends on their chemical composition, structure, particle size, and specific surface area (Zhdanov, 2013; Laassiri et al., 2014).

Mixed-metal oxides play a relevant role in this kind of application, as well as in many areas of chemistry, physics, and materials science (Wachs, 2005). The combination of two metals in an oxide matrix can produce nanoscale materials with novel structural or electronic properties, culminating in superior performance during technological applications (Tavakoli et al., 2007). The most often used materials can adsorb oxygen and generate reactive oxygen species that oxidize soot (Legutko et al., 2013). Numerous studies in this field have focused on mixed oxides, which exhibit significantly enhanced thermal stability, redox properties, and catalytic activity (Guillén-Hurtado et al., 2012; Liu et al., 2011; Krishna et al., 2007). The redox reaction disturbs the charge balance of the mixed-valence binary oxides, but the creation of oxygen vacancies ensures electroneutrality (Bensaid et al., 2013). Ceria can successfully abate pollution as a result of its elevated oxygen transport capacity and its ability to shift easily between reduced and oxidized states ($\text{Ce}^{3+}/\text{Ce}^{4+}$) (Trovarelli and Fornasiero, 2013).

Nevertheless, thermally severe operation conditions in the automotive engine system can lead to significant loss of surface area as well as CeO_2 thermal and chemical deactivation (Fernandes et al., 2009; Kärkkäinen et al., 2013). Catalyst deactivation detected along time stems mainly from CeO_2 sintering and segregation on the catalyst surface, suggesting that ceria has poor thermal stability (Hernández-Giménez et al., 2013). Formation of CeO_2 -based mixed oxides usually improves the thermal stability and catalytic activity of the final materials (Wang et al., 2012a,b). CeO_2 -doped metal oxides possess enhanced oxygen exchange capacity arising from creation of structural defects. A larger amount of oxygen vacancies originate in the structure of the mixed oxide, increasing the soot combustion rate. These oxygen vacancies are point defects in the CeO_2 lattice structure that determine the CeO_2 oxygen storage capacity, redox potential, and oxygen mobility (Bueno-López, 2014; Aneggi et al., 2014; Han et al., 2014; Zhao et al., 2008; Farmer and Campbell, 2010). Recently, transition metals (such as cobalt, copper, and iron) supported on/or doped into CeO_2 -based mixed oxides have been shown to display strong soot oxidation activity via a redox-type mechanism assisted by oxygen spillover on CeO_2 or a synergistic effect between the transition metal oxides and CeO_2 (Katta et al., 2010; Wu et al., 2010; Harrison et al., 2003; Gálvez et al., 2013). Also, it has been found that metal/ceria interactions induced by interface contacts between the two components strongly affect their redox properties and their catalytic properties (Shih et al., 2014; Wei et al., 2012).

CuO is an important p-type semiconductor with application in solar energy cells, electronics, gas sensors (Zhang et al., 2014; Brillson and Lu, 2011), inorganic pollutants removal (Ali, 2012; Bahrami et al., 2014), biosensors, magnetic storage media, optical switch, batteries, and heterogeneous catalysis (Rao et al., 2011). CuO is one of the most prominent

catalysts and has extensive use in environmental catalysis. A large number of investigations on CuO-ceria catalysts preparation have been carried out to obtain a catalyst with intimate interface, which is the reason for their high efficiency in oxidation reactions (Zhang et al., 2014). Furthermore, copper-based catalysts are environmentally compatible and economically advantageous. Generation of oxygen vacancies in the CeO_2 support enhances the catalytic performance of copper oxide in oxidation reactions because these vacancies allow for higher oxygen mobility and diffusion from the lattice to the interface of copper oxide and ceria (Rao et al., 2011). Incorporation of copper ions into the ceria lattice promotes structural defects and improves cerium reducibility, resulting in higher degree of oxygen adsorption and improved performance in soot oxidation (Nascimento et al., 2014b).

This paper describes the preparation of $\text{Ce}_{0.6}\text{Cu}_{0.4}\text{O}_2$ mixed binary oxide over cordierite substrates by the sol-gel method and evaluates the catalytic activity of the supported mixed oxide in diesel soot particulate oxidation.

2. Experimental

2.1. Preparation of the mixed oxide deposited on cordierite

In a typical procedure, a simple sol-gel method was adopted to prepare $\text{Ce}_{0.6}\text{Cu}_{0.4}\text{O}_2$ mixed oxides. The mixed oxides were synthesized from a mixture of cerium(III) nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99% Fluka) and copper(II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 99% Acros). The starting materials were dissolved in ethanol, and the Ce/Cu molar ratio in the ethanolic solution was 3:2; the final Ce^{3+} concentration was 0.4 mol L^{-1} . The mixture was heated under reflux with successive additions of $200 \mu\text{L}$ of D,L-lactic acid (85% Acros), until a stable green-blue sol emerged. To obtain the powder catalysts, the sol was dried until ethanol was eliminated. Finally, some portion of the catalyst was further calcined at 650°C for 3 h under air atmosphere, to eliminate the residual organic material (Nascimento et al., 2014a). Pure CeO_2 was also prepared for further comparisons; the same sol-gel method was adopted but in the absence of the copper precursor.

The cordierite honeycomb substrates ($5\text{SiO}_2 \cdot 2\text{Al}_2\text{O}_3 \cdot 2\text{MgO}$, Umicore®, Brazil) with $4.4 \text{ m}^2 \text{ g}^{-1}$ specific surface area (SSA) were coated with the $\text{Ce}_{0.6}\text{Cu}_{0.4}\text{O}_2$ sol by the impregnation method. The coating process consisted of immersing the ceramic substrate into the $\text{Ce}_{0.6}\text{Cu}_{0.4}\text{O}_2$ sol at 50°C for 5 min, followed by oven drying at 70°C with subsequent heating at 650°C for 3 h; this procedure was repeated four times (Nascimento et al., 2014c). The catalyst mass that adhered to the monolith after impregnation was gravimetrically determined for each preparation by weighing the vacuum-dried cordierite samples before and after the impregnation procedure. The amount of loaded catalyst was 5% in mass with relation to the initial mass of the substrate.

2.2. Catalyst characterization

Structural characterization of the catalysts (powder) was conducted on a Siemens D5005 X-ray diffractometer (XRD) operating with a copper tube ($\text{Cu-K}\alpha$ radiation, 1.541 \AA) under voltage of 40 kV and current of 30 mA; the 2θ values ranged from 20° to 90° . To monitor H_2 consumption, temperature-programmed reduction (H_2 -TPR) of $\text{Ce}_{0.6}\text{Cu}_{0.4}\text{O}_2$ deposited on

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