

Catalytic combustion of soot over Ru-doped mixed oxides catalysts

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Received 21 November 2013; revised 27 February 2014

Abstract: We employed modified substrates as outer heterogeneous catalysts to reduce the soot originating from the incomplete diesel combustion. Here, we proposed that ceria (CeO_2)-based catalysts could lower the temperature at which soot combustion occurred from 610 °C to values included in the operation range of diesel exhausts (270–400 °C). Here, we used the sol-gel method to synthesize catalysts based on mixed oxides ($\text{ZnO}:\text{CeO}_2$) deposited on cordierite substrates, and modified by ruthenium nanoparticles. The presence of ZnO in these mixed oxides produced defects associated with oxygen vacancies, improving thermal stability, redox potential, sulfur resistance, and oxygen storage. We evaluated the morphological and structural properties of the material by X-ray diffraction (XRD), Brumauer-emmett-teller method (BET), temperature programmed reduction (H_2 -TPR), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). We investigated how the addition of Ru (0.5 wt.%) affected the catalytic activity of $\text{ZnO}:\text{CeO}_2$ in terms of soot combustion. Thermogravimetric analysis (TG/DTA) revealed that presence of the catalyst decreased the soot combustion temperature by 250 °C, indicating that the oxygen species arose at low temperatures, which was the main reason for the high reactivity of the oxidation reactions. Comparative analysis of soot emission by diffuse reflectance spectroscopy (DRS) showed that the catalyst containing Ru on the mixed oxide-impregnated cordierite samples efficiently oxidized soot in a diesel stationary motor: soot emission decreased 80%.

Keywords: soot combustion; ceria; mixed oxides; ruthenium nanoparticles; rare earths

The hazardous nature of diesel soot, has led researchers to develop devices that can diminish, soot emission from engines, in the hope that new technologies will help remedy the problems caused by soot^[1,2]. One strategy to diminish soot emission has been to design catalytic filters or traps that combine soot retention and combustion^[3–5]. These catalytic filters should perform well at these low temperatures, because the exhaust gases usually cool down to 270–400 °C. Many catalysts mixed with metal oxides and noble metals can function as traps. The most often used materials can adsorb oxygen and generate reactive oxygen species, which oxidize soot^[6–8]. The most active oxides for soot combustion contain metals, which can perform redox cycles during the soot combustion process. The redox process disturbs the charge balance of the mixed-valence binary oxides, and electroneutrality is ensured by creation of oxygen vacancies. Several kinds of catalysts have been tested, such as oxides^[9–15], mixed oxides^[16–19], alkaline or heavy metal oxides^[20–24], and precious metals^[25–29].

The ability of ceria (CeO_2) to undergo reduction and reoxidation is important for a number of catalytic applications^[30–33]. Oxygen vacancies exist in CeO_2 because many $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox sites are rapidly formed and removed, which results in remarkable oxygen storage capacity^[33]. This function is called oxygen storage/release

capacity. In more general terms, it is referred to as redox and oxygen-vacancies behavior; it accounts for the characteristics of the CeO_2 reduction and oxidation processes, confirming that these materials generate oxygen active species that consume soot^[34,35]. However, thermally severe conditions of use in the automotive engine system lead to significant degradation including surface area loss and deactivation of CeO_2 ^[37,38]. The performance of ceria in automotive catalysts can be enhanced by doping this oxide with a second metal (Zr, V, Cu, Co, Au, Pt, Tb, La, Mn)^[39–45]. The improvement in the catalytic properties of ceria in mixed oxide is likely associated with an enhancement in the thermal stability and reducibility of the ceria. One particularly interesting system is that of ceria-titania, with several reports indicating that titania doping leads to improved reducibility^[46]. The combination of two or more metal oxides on the surface of a support produces a complex system with multiple functions stemming from each oxide, which often gives rise to new properties. Zinc oxide (ZnO) is a semiconductor with potential use as filler selection in composites — it has versatile properties (chemical stability, low dielectric constant, high luminous transmittance, high catalytic activity, antibacterial effect, intensive ultraviolet, and infrared absorption), easy preparation and low cost^[47], making it potentially applicable in UV absorption^[48],

Foundation item: Project supported by the National Council for Scientific and Technological Development (CNPq) (105477/2012-5)

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DOI: 10.1016/S1002-0721(14)60116-2

catalyst^[49,50], gas sensor^[51,52], photocatalyst^[53], and additive in many industrial products^[54].

The incorporation of zinc ions into the ceria lattice promotes structural defects and improves ceria reducibility, resulting in higher degree of oxygen adsorption and, consequently, improves performance in soot oxidation. Therefore the formation of oxygen vacancies in the ZnO phase favors the reducibility of the ceria phase. This mechanism, formation of an oxygen vacancy in the ZnO phase that is further oxidized by the reduced ceria phase, accounts for the synergy between both phases^[55]. Thus ZnO can react with ceria to form mixed oxides, elicits defects associated with oxygen vacancies, whereas Ce that forms eutectics with Zn produces defects associated with zinc vacancies^[56]. Annealing ZnO-CeO₂ interfaces can induce new interface chemistry that provides additional effect.

The addition of noble metals such as Au, Pt, Pd and Rh to mixed oxide increases the reactivity of catalyst, because it enhances the reducibility of these oxides at low temperature, and the oxygen exchange capacity of the oxides and raises the rate of soot the combustion. This happens because O₂ adsorbs onto the catalysts, subsequently increasing the mobility of active oxygen species^[57-60].

The association of ruthenium species with ceria is particularly interesting: it establishes a successful catalytic system in oxidation reactions, as compared with other noble metals^[61-69]. However, there are no studies on the catalytic activity of ruthenium-doped zinc-ceria binary oxides highlighting an electronic interaction between Ru and ZnO:CeO₂ toward the combustion of carbonaceous materials at low temperatures. Ruthenium can interact with CeO₂ in the following ways: Ru transfers electron to ZnO:CeO₂, and then ZnO:CeO₂ transfers oxygen to Ru, which contributes to soot combustion and effectively reduces emissions from diesel engines^[70]. Although Ru is not used as an active element of three-way catalyst (TWC) because of volatile property and very low melting point of RuO₄^[70] when the temperature is higher than 800 °C. Elementary analysis on Ru-CeO₂ before and after tests showed that there was no Ru loss even after 10 cycles below 800 °C^[71], it will be a good model for a mechanistic study on the interaction of precious metals on CeO₂-based supports and how this interaction translates into a significant catalytic activity toward the combustion of soot. In this paper, we prepared the mixed binary oxide ZnO:CeO₂ over cordierite by the sol-gel method and evaluated how Ru nanoparticles affected the properties of the supported mixed oxide, we verified the catalytic activity of the most promising materials in diesel soot oxidation.

1 Experimental

1.1 Preparation of the sol-gel mixed binary oxide and powder

The solid system ZnO:CeO₂ was synthesized from a

mixture of zinc nitrate (Zn(NO₃)₂·6H₂O, 98% Acros) and cerium(III) nitrate (Ce(NO₃)₃·6H₂O, 99% Fluka); the Zn/Ce molar ratio in the ethanolic solution was 3:2; and the final M⁺ concentration was 0.4 mol/L, as described^[72]. The mixture was heated under reflux with successive additions of 200 μL of lactic acid (85%), until the suspension totally dissolved and a stable and transparent sol (A) arose. To obtain the powder catalysts, the sol was dried until ethanol was eliminated. The powder was calcined at 650 °C for 3 h under air atmosphere, to completely remove the organic material.

1.2 Preparation of the Ru nanoparticles microemulsion and the Ru/ZnO:CeO₂ powder

Incorporation of Ru into the ZnO:CeO₂ mixed oxide was accomplished using a water-in-oil microemulsion^[73-75] composed by H₂O (12 wt.%), Brij 30 as surfactant (polyethyleneglycoldodecylether, 23 wt.%), and *n*-heptane (65 wt.%) as non polar phase. Microemulsions were prepared by adding 5.1 g of a 0.122 mol/L aqueous solution of the metal precursor (RuCl₃·*n*H₂O, 99% Aldrich) to a mixture of *n*-heptane (28.2 g) and Brij 30 (10.0 g), under stirring, at a controlled temperature of 40 °C. Another microemulsion containing 2.5 mol/L sodium borohydrite (NaBH₄, 98% Aldrich) in the aqueous phase was also prepared and carefully (strong reaction) added to the solution containing the metal salt, under constant stirring for 30 min at 40 °C (B).

The mixed binary oxides powder (3.0 g) was dispersed (5 min at ~25 °C) into 20 mL of a microemulsion containing Ru nanoparticles (B). The resulting catalyst was washed with water and ethanol, and dried in a vacuum oven at 70 °C for 3 h. The Ru concentration in the studied samples was assayed by flame atomic absorption spectroscopy (FAAS) and energy dispersive X-ray spectrometry (EDS).

1.3 Preparation of the ZnO:CeO₂/cordierite and Ru/ZnO:CeO₂/cordierite catalysts

The cordierite ceramic substrates (5SiO₂·2Al₂O₃·2MgO, Umicore[®], Brazil) with cylindrical shape (11.5 cm in height and 10.5 cm in diameter), 100 cm² and 4.4 m²/g specific surface area (SSA) were modified using the ZnO:CeO₂-impregnation method^[72]. To this end, the substrates were cut into cylindrical pieces (3.5 cm height and 2.5 cm diameter), for the use in the catalytic tests. Oxides were deposited by immersing the ceramic substrate into the ZnO:CeO₂ sol (A) at 50 °C for 5 min, followed by heating at 650 °C for 3 h; this procedure was repeated four times.

The mass of catalyst that adhered to the monolith after the impregnation procedure was gravimetrically determined for each preparation. To this end, the vacuum-dried cordierite samples were weighed before and after the impregnation procedure. The amounts of loaded

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