



# Effects of preparation and structure of cerium-zirconium mixed oxides on diesel soot catalytic combustion

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## ABSTRACT

Mixed oxides of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  ( $0.1 \leq x \leq 0.9$ ) were prepared by sol-gel method, in aqueous ammonia solution with  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$  and  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  as precursors, and employed in diesel soot combustion. The catalysts were characterized by XRF/EDX, nitrogen adsorption, TGA/DTG, powder XRD, FTIR/DRIFTS and Raman. In addition, the acidity was evaluated by adsorption and desorption of pyridine. XRD indicated the formation of solid solutions that progressively distorted from cubic into tetragonal lattices. Raman studies confirmed that the Ce–O bonding was stronger in the mixed oxide series because of the cell contraction, as a result of the zirconium insertion.  $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$  was the most acidic and active material, shifting the combustion temperature ( $T_m$ ) from 622 to 547 °C (loose contact) or 404 °C (tight contact). The calculated activation energy for the catalytic combustion of this optimized oxide attested that the combustion temperature was lower under all conditions, compared to the thermal process. The catalyst was utilized five times without any appreciable loss of activity and maintained its structural properties.

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## 1. Introduction

Research aimed to solve the ambient pollution caused by emission of diesel soot particulates is currently one of the most difficult tasks. One of the challenges is to regenerate the catalyst in the diesel filter to retain particulate (DPF), as this device undergoes broad reaction conditions for regeneration. Another drawback is the slow reaction process due to the loose contact between the particulates and the catalyst. The low mobility and relative high diameter ( $d_p$ ) between 10 and 100 nm inhibit its penetration in microporous catalysts [1,2]. Moreover, there is a wide variation in the temperature of exhausted gases (200–600 °C), depending on the motor design and power output [3]. Therefore, an efficient catalyst must work at low temperatures and be thermally stable for regeneration purposes.

In the mid 1970s, the technology of three-way catalysts (TWC) symbolized a major breakthrough in the development of devices for automotive pollution control [4,5]. The devices consisted of  $\text{CeO}_2$  as the main component to promote oxygen storage and release capacity (OSC), which is closely related to the efficiency of TWC system [4,5]. Another breakthrough was the advent of new pro-

motors based on  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  mixed oxides. It was discovered that these solid solutions improved the thermal stability and OSC of the TWC [4]. One of the key properties of these promoters is the fast redox cycle of  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$  and the high mobility of  $\text{O}^{2-}$  ions in the lattice of ceria compounds [6]. Thus, studies on oxides are very relevant for understanding their fundamental characteristics and suitability in the automotive industry.

Preparation of mixed oxides of different proportions of Ce:Zr results in materials with tunable properties compared to  $\text{CeO}_2$  or  $\text{ZrO}_2$ . They show high thermal stability, oxygen storage, fluidity, and mobility in a modified lattice [7–11]. These enhanced properties can be related to the structure of the mixed oxide. The substitution of Ce by Zr is considered a modification of the  $\text{CeO}_2$  lattice upon insertion of zirconium, because of the smaller size of  $\text{Zr}^{4+}$  (84 pm) versus  $\text{Ce}^{4+}$  (97 pm). Increasing the amount of Zr, the  $\text{CeO}_2$  lattice (cubic fluorite structure,  $Fm\bar{3}m$  space group) distorts to form tetragonal  $P4_2/nmc$  space group ( $t''$ ,  $t'$  and  $t$ -phase) [12–14]. Accordingly, no well-defined frontiers between these phases exist, as the distortion continuously changes with sample composition. In addition, this distortion is sensitive to the particle size of the mixed oxide [5].

It is known that different preparation methods of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  lead to materials with variable structure and physico-chemical properties [15,16]. For instance, nanotubes of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  were prepared using membrane templates of polycarbonate leading to a mixture of phases (cubic and tetragonal), when  $x = 0.5$ , 0.7 and 0.9 [15]. In another work, the mixed oxides were synthesized by sol-gel method, and different phases were observed, such as cubic ( $x = 0.16$ )

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