

## Black carbon oxidation activity of ceria nanoparticles doped with zirconium

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### Introduction

Black carbon (BC) as a solid core of particulate matter, or soot, has been associated with human health, pollution and climate concerns [1]. The transportation sector accounts for 52 % of the total North America BC emissions and about 93% of this total come from diesel sources [1]. Diesel Particulate Filter (DPF) is an effective technology for controlling the emission of soot particles from diesel engines, but active regeneration at high temperature is required to oxidize accumulated soot. The Catalyzed DPF (CDPF), an alternative approach, can be regenerated at lower temperatures, but the commercial ones are typically coated with platinum group metals (PGM) that are costly and sensitive to sulphur. Therefore, a variety of PGM-free catalytic systems for soot oxidation have been studied in order to develop a low temperature catalyst for the CDPF application.

Cerium oxide is known to be active in BC oxidation due to its ability to produce active oxygen species [2] and facilitate the movement of those species to the catalyst/BC interface [3]. Substitution of cerium with various cations can improve its bulk redox properties and oxygen mobility that can result in enhanced catalytic activity. In addition, soot oxidation takes place on the soot/catalyst interface; therefore high surface area might be beneficial for the overall activity of the process. Several methods have been developed to prepare nanocrystalline oxide powders with relatively high surface area. In this study, Zr-CeO<sub>2</sub> nanoparticles were synthesized by two different methods and the effect of preparation methods on the structural and catalytic properties in BC oxidation reaction was investigated.

### Materials and Methods

Zr-CeO<sub>2</sub> (30 wt% of ZrO<sub>2</sub>) nanocrystalline oxides were prepared by co-precipitation and citric acid (CA)-assisted sol gel method. Cerium (3+/4+) nitrate and zirconyl nitrate aqueous solutions were used as precursors in both methods.

In the co-precipitation method, the precursor solutions were mixed and then added dropwise to a basic water solution while pH 10 was maintained with addition of ammonium hydroxide solution.

In the sol gel method, CA used as a chelating agent, was added to the initial precursor solution, and then the mixture was heated until a viscous gel was formed. For both methods, the final catalyst was obtained by drying followed by calcination at 550°C.

The activity of catalysts was evaluated by running Temperature Programmed Oxidation (TPO) experiments using tight contact between catalyst and carbon and a 30:1 w/w ratio. Carbon Black from Cabot was used as a model of BC. The carbon oxidation was performed with 10% O<sub>2</sub> in He flow, ramping the temperature to 800°C. The temperature corresponding to the maximum in TPO profile was selected as a measure of catalytic activity.

### Results and Discussion

T<sub>max</sub> in TPO profiles and surface area of the synthesized catalysts are presented in Table 1. Zr-CeO<sub>2</sub> catalysts prepared by co-precipitation showed higher activity than commercial Zr-CeO<sub>2</sub> mixed oxide that has been correlated to a higher surface area (76-95m<sup>2</sup>/g and 30m<sup>2</sup>/g, respectively). The most active oxide was synthesized using Ce<sup>4+</sup> precursor. This may be due to the facilitation of the integration of Zr<sup>4+</sup> into the CeO<sub>2</sub> structure when Ce<sup>4+</sup> is used in the preparation [4]. Zr-CeO<sub>2</sub> catalysts, synthesized from the same Ce precursor using different molar ratios of CeO<sub>2</sub> to ZrO<sub>2</sub>, showed that T<sub>max</sub> increased as the CeO<sub>2</sub> content decreased while the surface area remained constant. These results indicate that surface area alone cannot explain the differences in activities, and the amount of cerium in mixed oxides is a key factor controlling the catalytic performance.

**Table 1.** Activity and BET surface area of Zr-CeO<sub>2</sub> catalysts

Catalyst	ZrO <sub>2</sub> :CeO <sub>2</sub> W/w ratio	Preparation Method	Cerium Precursor	T <sub>max</sub> (°C)	BET Surface Area (m <sup>2</sup> /g)
CeO <sub>2</sub>		Commercial		491	34
Zr-CeO <sub>2</sub>		Commercial		503	30
Zr-CeO <sub>2</sub>	30:70	Co-precipitation	Ce <sup>3+</sup>	480	76
Zr-CeO <sub>2</sub>	30:70	Co-precipitation	Ce <sup>4+</sup>	453	95
Zr-CeO <sub>2</sub>	50:50	Co-precipitation	Ce <sup>4+</sup>	480	85
Zr-CeO <sub>2</sub>	70:30	Co-precipitation	Ce <sup>4+</sup>	517	91
Zr-CeO <sub>2</sub>	30:70	CA sol gel	Ce <sup>3+</sup>	453	55
Zr-CeO <sub>2</sub>	30:70	CA sol gel	Ce <sup>4+</sup>	451	83

Zr-CeO<sub>2</sub> catalysts synthesized by CA-assisted sol gel attained the lowest overall T<sub>max</sub> values of ~ 450°C regardless of the type of cerium precursor used, probably due to mixing of the metal ions at the atomic level during sol gel synthesis that led to a more uniform distribution of Zr in CeO<sub>2</sub> lattice. The high activity of these catalysts prepared by two different methods suggests a synergetic effect between Zr and Ce on BC oxidation.

### Conclusion

CA-assisted sol gel and co-precipitation are effective synthesis techniques for producing Zr-CeO<sub>2</sub> catalysts with relatively high BET surface areas and activity (T<sub>max</sub> ~450 °C) for soot oxidation. It was shown that the composition and structural properties of catalysts are key factors that can influence the carbon oxidation activity.

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### Reference

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