

# Reaction Mechanism in Catalytic Soot Combustion with CeO<sub>2</sub> Catalysts.

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## Introduction

Diesel soot elimination is a very difficult problem. The catalytic filters seems to be one of the technological alternatives in order to trap and burn the soot, at the exhaust gas temperature. In order to advance in a rational catalyst design, the reaction mechanism must be understood. In spite of this need, and even though there are many papers in the field, detailed studies regarding soot combustion mechanism are scarce, and the real kinetic is not typically reported. In most of these works a power-law rate expression was used to fit the experimental data [1].

In this study, we report data using ceria as catalyst for soot combustion, with the objective of obtaining a more realistic model for this reaction. Combining temperature programmed oxidation (TPO) analyses using different heating rates (HR) and final temperatures, and characterization techniques, it was possible to observe transient phenomena during soot combustion that provided new insights on reaction mechanism.

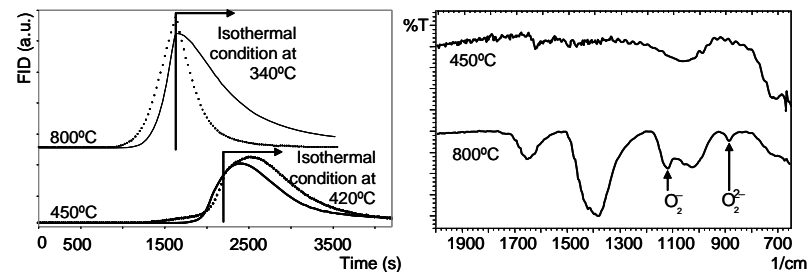
## Materials and Methods

Cerium (IV) oxide powder (< 5 micron), 99.9% (Aldrich) was calcined at 450°C and 800°C. Activity was measured by TPO analysis [1] of mechanical mixtures of soot with the catalyst (tight contact). The HR used was 4, 8, 12 and 16°C/min. Some TPO analyses were carried out holding different final intermediate temperatures (partial burnt tests). Catalysts were characterized by Fourier-Transformed Infrared Spectroscopy, X-Ray Diffraction, High Frequency CO<sub>2</sub> pulses, Differential Scanning Calorimetry, and X-Ray Photoelectron Spectroscopy. Kinetic parameter determination and simulations were made with MicroMath® Scientist® for Windows™ software.

## Results and Discussion

In Figure 1 partial burnt test are shown (dotted lines). It can be seen that for ceria calcined at 450°C, the reaction rate kept increasing even though the temperature remains constant at 420°C. This behavior was also observed at other intermediates temperatures (not shown). This phenomenon cannot be seen when the calcination temperature was 800°C (only the curve at 340°C is shown). It is interesting to note that the catalyst calcined at higher temperature has better activity. This kinetic result clearly show that the power-law kinetic model, although useful in some cases, does not represent the real mechanism.

FTIR spectra analyses reveal interesting differences between these catalysts (see Figure 2). After calcination at 800°C, bands assigned to O<sub>2</sub><sup>-</sup> y O<sub>2</sub><sup>2-</sup> [4] appear in the spectra of CeO<sub>2</sub> while these bands are not observed when the catalyst was calcined at 450°C. Additional results were obtained with SEM (partial burnt experiments), DSC, and TGA.



**Figure 1.** TPO profiles (partial burnt tests) at different final temperatures. Dotted line experimental data, full line simulated data.

**Figure 2.** FTIR spectra for CeO<sub>2</sub> calcined at different temperatures

Based on these results, a mechanism involving the following steps was considered:



In the first step the superoxide formation is proposed followed by peroxide formation from superoxides (second reaction), and then these species react with carbon (third reaction). The differences in activity pattern shown in Fig. 1 are attributed to these oxygenated species.

Kinetic parameters corresponding to ceria calcined at 450°C were obtained from a TPO run from room temperature up to 600°C. For the catalyst calcined at 800°C parameter estimation was done only for reaction (1) and (2), assuming that the parameter for reaction (3) are the same as for the catalyst calcined at 450°C. This means that the main difference between these two materials, is the initial availability of peroxide and superoxide. When these intermediates are not present in the catalyst, the typical behavior with a maximum reaction rate at constant temperature is displayed (Fig. 1). The simulations shown in Fig. 1 indicate a very good capacity prediction of this model, and help in the understanding of the phenomena involved in this mechanism.

## Significance

These findings helps in the advancement towards a rational catalyst design. In addition, in order to properly estimate the reaction rate for soot oxidation at constant temperature, such as in a working filter, the availability of realistic models are needed, and the one we found in this work largely improves the prediction capacity of the known models.

## References

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