

Catalytic Soot Oxidation: Effect of Ceria-Zirconia Catalyst Particle Size

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ABSTRACT

Catalysts that have been extensively investigated for direct soot oxidation in Catalyzed Diesel Particulate Filters (CDPFs) are very often based on mixed oxides of ceria with zirconia, materials known to assist soot oxidation by providing oxygen to the soot through an oxidation-reduction catalytic cycle. Besides the catalyst composition that significantly affects soot oxidation, other parameters such as morphological characteristics of the catalyst largely determined by the synthesis technique followed, as well as the reagents used in the synthesis may also contribute to the activity of the catalysts. In the present work, two ceria-zirconia catalyst samples with different zirconia content were subjected to different milling protocols with the aim to shift the catalyst particle size distribution to lower values. The produced catalysts were then evaluated with respect to their soot oxidation activity following established protocols from previous works. A previously developed multi-population kinetics model was employed to describe quantitatively the soot oxidation process and assess the effect of catalyst particle size (for each composition) on the kinetic parameters. In general, the intrinsic reactivity of a given catalytic material can be significantly enhanced through appropriate morphological and structural modulation. Such a step is a prerequisite for any subsequent development of CDPFs based on any catalytic material.

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INTRODUCTION

Ceria-Zirconia mixed oxides are well known catalysts that find application in several technological fields and are widely implemented in the area of Diesel soot oxidation [1, 2, 3, 4, 5, 6]. Two different ceria-zirconia catalysts were evaluated within the current work in order to study the effect that different compositional, morphological and structural characteristics have in catalytic soot oxidation. Both catalysts can be produced in large quantities by industrial synthesis methods. Their main difference lies in their composition, as they are mixtures of ceria/zirconia in two different ratios. The two catalysts were subjected to a series of milling protocols where the only parameter altered was the milling duration with the aim to alter their characteristics and affect their catalytic activity [7]. In order to determine the effect that milling has on the existing crystal phases and crystallite sizes comparative X-Ray diffraction analysis were performed on both the initial catalysts and the respective milled products. The alterations on the morphological and structural characteristics of the catalysts were studied by SEM analysis. The catalytic soot oxidation activity of the samples was determined by Thermo-gravimetric analysis (TGA) performed on specific mixtures of the samples with soot following established protocols from previous works, e.g. [1]. TGA is a well-established

method to analyze carbonaceous materials and when properly applied can provide information on its oxidation [2, 3, 4]. The soot oxidation process can be depicted in Arrhenius coordinates, by plotting the instantaneous reaction rate vs the inverse of Temperature, for each catalytic material-soot combination. A previously introduced multi-population kinetics model [9, 10, 11] was employed to describe the soot oxidation rate quantitatively and assess the effect of catalyst particle size (for each composition) on the kinetic parameters. The latter values were calculated in an attempt to elucidate the mechanism of the catalytic soot oxidation. In general, the intrinsic reactivity of a given catalytic material can be significantly enhanced through appropriate morphological and structural modulation [12]. The present study is a continuation of the work initiated in [9] and is an effort to describe quantitatively catalytic soot oxidation kinetics, taking into account catalyst particle size.

EXPERIMENTAL PART

Mechanical Modification of the Raw Catalysts

Two different oxides of ceria-zirconia mixed oxides were obtained by an industrial partner of our laboratory. The two samples had different ceria /zirconia ratios, namely: 28.7/71.3wt% and 66.7/33.3wt%.

Henceforth the first material will be denoted as Zr-rich catalyst and the second as Ce-rich catalyst. The two catalysts were milled with an in-house developed ball mill for periods ranging from 0-40 hours. Since the Ce-rich catalyst after 40 hrs of milling exhibited a Sauter mean diameter (SMD) $\sim 15\%$ higher than the respective sample obtained from the Zr-rich catalyst, the Ce-rich sample was further milled for a total of 72 hours in order to study if smaller particle sizes can be obtained upon increase of milling duration. During ball-milling, an aqueous slurry of the powder is placed within cylindrical vessels with a certain amount of grinding media, in this case zirconia balls were used as grinding media. The grinding vessels are then set on a pair of rotating axes where the powder is milled during its rotation. The whole process is based on the principle of impact and attrition caused by the grinding balls, as they move within the rotating vessel. This procedure is extensively used to produce fine powders in several applications among which is treatment of ceramic powders.

Characterization of the Catalysts

X-ray Diffraction (Siemens D500/501) and Scanning Electron Microscopy (JEOL JSM-6300) were employed for the characterization of the materials phases. From the X-ray diagrams, the crystallite size of the materials was calculated by employing the Scherrer equation for the main peak of the detected Ce-Zr mixed phase (at 29.5° and 29° respectively for the Zr-rich and Ce-rich catalysts). The specific surface area measurements were determined by nitrogen adsorption by means of an Autosorb-1 instrument and the corresponding specific outgassing temperature was 150°C . The BET surface area is calculated from the BJH Adsorption/Desorption cumulative surface area of pores and average pore width respectively. The Sauter mean diameter ($d_{3,2}$) of the samples was measured by a laser ensemble diffraction method (Malvern Mastersizer).

Mixtures of the catalysts with a reference soot, a flame-generated carbon black (Statex, N330), were prepared at a ratio of 2:1 (catalyst: soot). This soot contains no mineral impurities, and provides a reference material used extensively at our laboratory for initial screening studies of catalyst reactivity [11]. These were very well mixed together in an agate mortar to achieve a high degree of contact and were then placed in an alumina crucible and were transferred to a thermogravimetric analyzer (TGA, PYRIS 6, Perkin Elmer). The samples were heated under $20\% \text{O}_2$ in N_2 with a temperature increase rate of $3^\circ\text{C}/\text{min}$ from 150 up to 700°C .

EXPERIMENTAL RESULTS

Mechanical Modification of the Raw Catalyst Samples

Phase Composition and Crystallization

In Figure 1, the XRD patterns of the two raw catalysts (prior to milling) are compared. Both samples exhibit similar peaks, which shift to higher angles as the zirconia content increases - something that might indicate

the formation of a solid solution between the two oxides. From the XRD diagrams the crystallite size of all samples was calculated by employing the Scherrer equation for the main phase of Ce-Zr mixed oxides. Their values are summarized in Table 1. Both of the catalysts studied in this work, irrespectively of their composition exhibit similar crystallite size that lied in the range of $\sim 60\text{\AA}$.

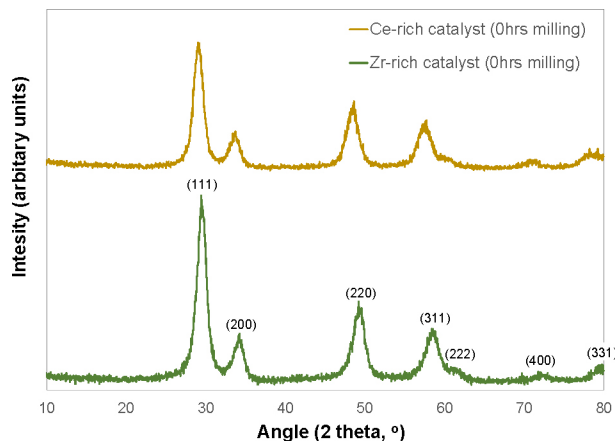


Figure 1. Comparative XRD patterns of the two raw (not-milled) Ce-Zr catalysts.

In Figure 2 and Figure 3, comparative XRD diagrams of the samples deriving from the Zr-rich and the Ce-rich catalyst respectively after different milling periods are presented. As it can be seen from the comparative diagrams in both cases, the milling procedure followed does not have any effect on the phase composition and crystallization of the materials. Using similar calculations to the calculations performed in the diagrams of Figure 1, the crystallite size of all samples analyzed by XRD was calculated. When comparing the crystallite values of the different grades, it is observed that both catalysts, irrespectively of their composition and the milling duration maintain their initial crystallite size of the raw catalysts, i.e. $\sim 60\text{\AA}$.

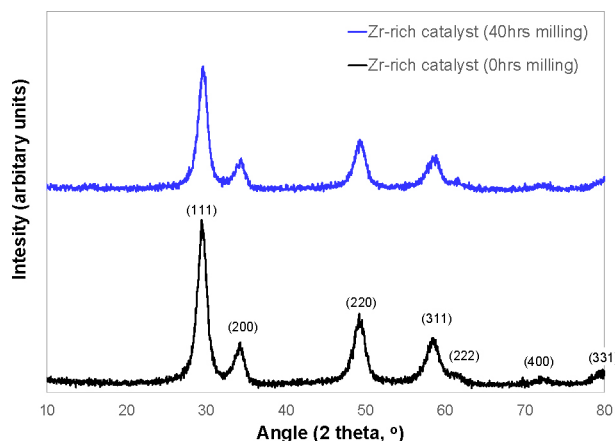


Figure 2. Comparative XRD patterns of the as received and the milled for 40hrs Zr-rich catalyst.

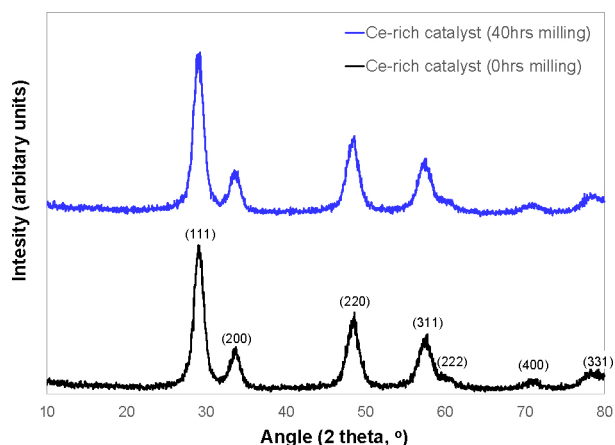


Figure 3. Comparative XRD patterns of the as received and the milled for 40 hrs Ce-rich catalyst.

Particle Size Distribution

In Figure 4 the particle volume probability density function of the raw Ce-rich and Zr-rich catalysts are depicted. In both cases the size distribution curves are very similar and exhibit a multimodal character, with a sub-micron mode and some supermicron modes. The Ce-rich catalyst contains a somewhat larger amount of supermicron particles, extending up to the 50 μm range.

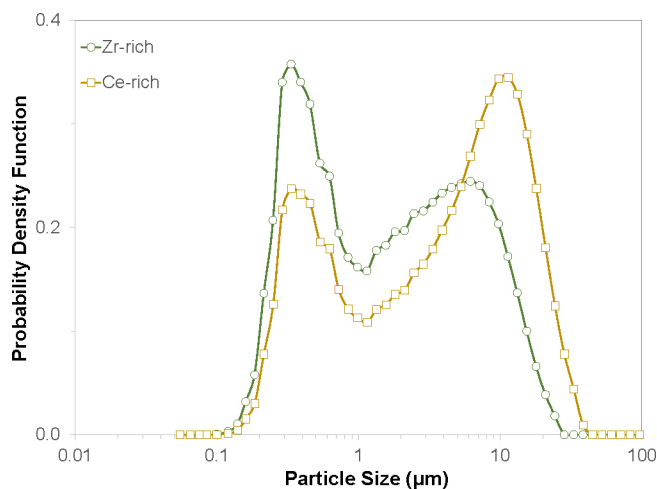
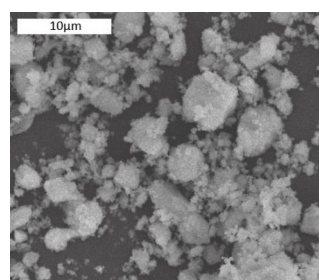
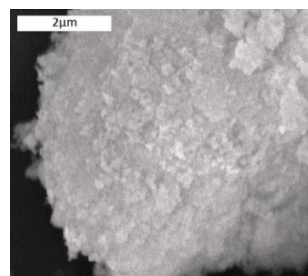


Figure 4. Comparative particle volume probability density function of the two raw Ce-Zr catalysts

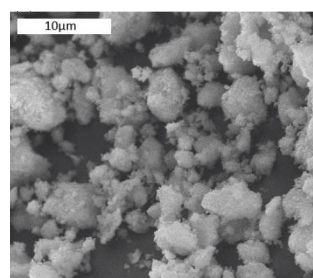
This observation is also supported from the images obtained by Scanning Electron Microscopy (SEM) of the two different samples. In the case of the Ce-rich catalyst, the larger particles dominate. In Figure 5, SEM images of the raw catalysts are shown, where also larger magnifications of the larger particles are shown, revealing more details about their morphology.



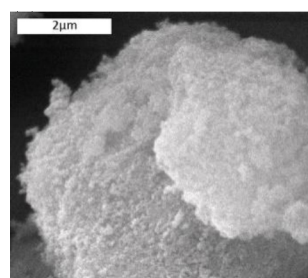
a.



b.



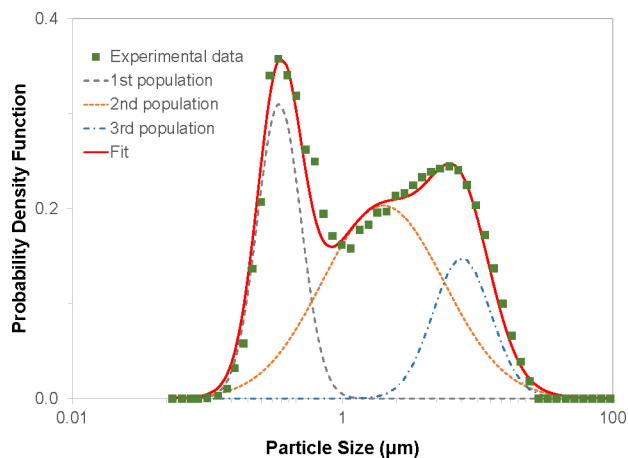
c.



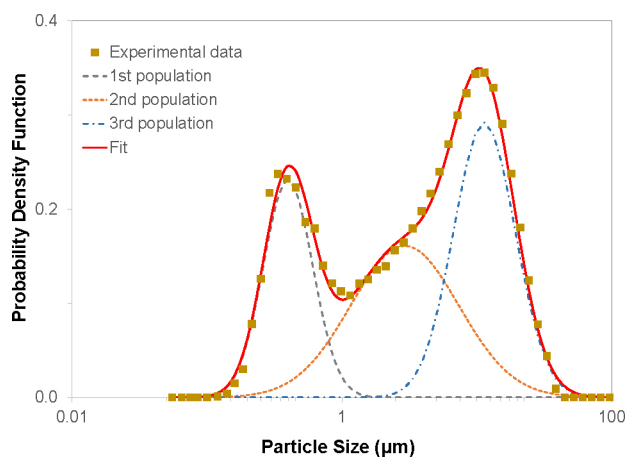
d.

Figure 5. Images from SEM received under a magnification of x3,000 and a magnification of x15,000 from the raw (a),(b) Zr-rich catalyst and (c), (d) Ce-rich catalyst respectively.

Further analysis of the raw particle size distributions reveal that these can be described very precisely as tri-modal log-normal distributions (Figure 6).



a.



b.

Figure 6. Three particle population log-normal distributions that describe the size distribution curves of the a) Zr-rich and b) Ce-rich raw samples

Effect of Milling Duration on Particle Size Distribution

The two Ce-Zr oxides were subjected to milling for the modification of their particle size. The duration of the milling was varied for both materials and the effect of the milling duration on the distribution of the particles is illustrated in Figure 7 and Figure 8 for the Zr-rich and the Ce-rich catalysts respectively (Ce-rich samples were subjected to additional milling up to 72 hours in order to achieve similar particle size distribution to that of the Zr-rich samples). In both cases the increase of the milling time causes a reduction of the large particles and a shift to smaller diameters.

When comparing the two catalyst materials after 40 h of milling (Figure 9) it is observed that the Ce-rich catalyst continues to maintain a higher population of supermicron particles, in accordance to the findings in the case of the non-milled samples. In an attempt to reduce the population of the larger particles found in the Ce-rich catalyst, the sample was further milled for an additional 32 hrs. The new sample (total milling time 72 hrs) did not exhibit any significant change in the particle size distribution although it was milled almost twice as long as the 40 hours sample (Figure 9).

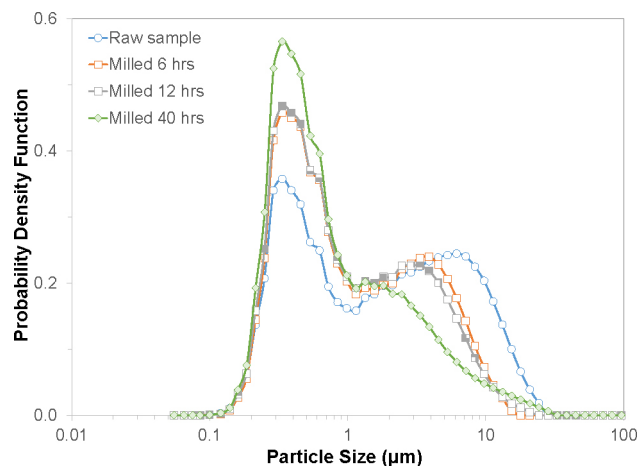


Figure 7. Comparative particle volume probability density function after milling for different durations of the Zr-rich catalyst.

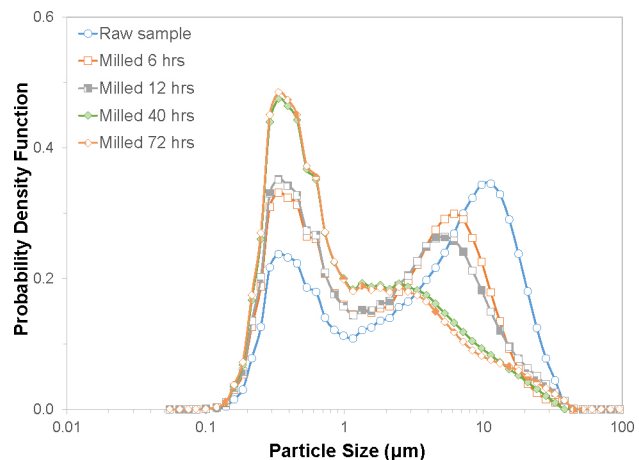


Figure 8. Comparative particle volume probability density function after milling for different durations of the Ce-rich catalyst.

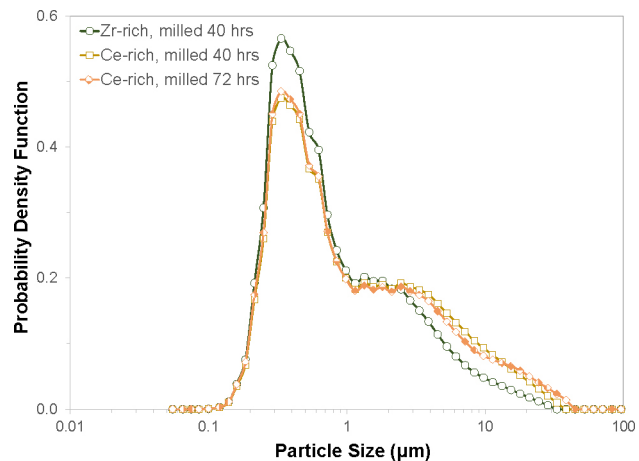


Figure 9. Comparative particle volume probability density function of the two Ce-Zr catalysts milled for 40 hours and the Ce-rich catalyst milled for 72 hours

These results are in general in agreement with the images obtained by SEM where the co-existence of fine, intermediate and coarse particles corresponding to a tri-modal distribution, is verified (Figure 10, indicative SEM images taken from the samples milled for 40 hours).