Thermally stable ceria–zirconia catalysts for soot oxidation by O\textsubscript{2}

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Abstract

Ce–Zr mixed oxides calcined at 1000 °C are more active catalysts for soot oxidation than pure CeO\textsubscript{2} calcined at the same temperature, both in loose and tight contact between soot and catalyst. 1000 °C sinterised-CeO\textsubscript{2} presents a very low surface area (2 m\textsuperscript{2}/g), a large crystal size (110 nm) and a lack of surface redox properties. Ce–Zr mixed oxides present higher BET surface areas (typically 17–19 m\textsuperscript{2}/g), smaller crystal sizes and enhanced redox properties. The Zr molar fraction does not affect appreciably the catalytic activity of Ce–Zr mixed oxides in the range studied (Zr molar fraction from 0.11 to 0.51).

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1. Introduction

One of the solutions to avoid the emission of soot produced by diesel vehicles is to trap the particles on a Diesel Particulate Filter (DPF) and burn soot periodically to prevent a pressure increase in the exhaust line [1,2]. In general, DPF is regenerated by post injection of fuel to raise the DPF inlet gas temperature. It has been extensively studied the regeneration of different filters made of highly stable materials such as cordierite or SiC among other substrates, and it has been observed [3] that the temperature inside the DPF can increase up to 1000–1100 °C as a consequence of the highly exothermal soot combustion process. Some authors suggest temperature gradients of 100 °C/cm along both radial and longitudinal directions of the DPF [3].

CeO\textsubscript{2} has been proposed as a promising soot oxidation catalyst to accelerate the soot-O\textsubscript{2} reaction [4–6]. In the presence of CeO\textsubscript{2}, it has been reported [4] that the gas-phase O\textsubscript{2} replaces lattice oxygen of CeO\textsubscript{2} creating highly active oxygen, which is able to react with soot. However, due to its tendency to deactivated at high temperatures, pure CeO\textsubscript{2} cannot be used alone, and there is a need for thermally stable materials which can withstand temperatures up to 1000 °C, eventually reached during regeneration. One approach previously used to stabilize ceria against sintering, making CeO\textsubscript{2}-based materials suitable for soot oxidation, was to dope it with other rare earth elements such as La\textsuperscript{3+} [7]. Ln\textsuperscript{3+} significantly improved the catalytic activity of CeO\textsubscript{2} (calcined at 1000 °C) for soot oxidation by O\textsubscript{2}, and this improvement was related to the increase in BET surface area and to the enhanced redox properties of La-doped ceria. It has been also recently reported [6] that CeO\textsubscript{2} doped with transition metals (Zr and Fe) and rare earth elements (La, Pr, Sm, and Tb) becomes a more active catalysts for soot oxidation by O\textsubscript{2}. In this publication [6], catalysts calcined at 500 and 750 °C were studied. An important decrease of CeO\textsubscript{2} activity after calcination at 750 °C was reported and Zr-doping enhanced the thermal stability and the oxygen storage capacity of pure ceria. In the mentioned study [6], the key role of oxygen storage capacity in soot oxidation was confirmed.

The goal of the current study is to analyse the catalytic activity of CeO\textsubscript{2}, ZrO\textsubscript{2} and Ce–Zr mixed oxides for soot oxidation by O\textsubscript{2}. The study is focussed on catalysts heat treated at high temperature (1000 °C), in order to evaluate...
the thermal stability of these materials and their catalytic activity after a potential exposure to the high temperatures eventually reached in a DPF.

2. Experimental

CeO$_2$, ZrO$_2$ and Ce$_{1-x}$Zr$_x$O$_2$ mixed oxides were prepared from Ce(NO$_3$)$_3$·6H$_2$O (Aldrich, 99.9%) and/or ZrO(NO$_3$)$_2$·nH$_2$O (Aldrich). The required amounts of these precursors (in order to reach different Ce/Zr molar compositions) were mixed in a mortar and calcined in static air at 1000°C for 90 min (heating rate 10°C/min).

X-ray diffractograms were recorded in a Bruker D8 diffractometer using Cu K$_\alpha$ radiation ($\lambda = 0.15418$ nm). Spectra were recorded between 10° and 70° (2θ) with a step of 0.02 and a time per step of 3 s. The average crystal sizes (D) were determined using the equations of Scherrer and Williamson–Hall.

In the Scherrer’s equation:

$$D = \frac{K \cdot \lambda}{\beta \cdot \cos \theta}$$

(1)

$\lambda$ is the X-ray wavelength, K is the particle shape factor, taken as 0.94 [8], $\beta$ was defined as the width at half maximum of the peak and $\theta$ is the position (angle) of the peak. For CeO$_2$ and Ce–Zr mixed oxides, the peak (111) of the cubic phase centred at about 28.7° was considered.

For CeO$_2$ and Ce–Zr mixed oxides, the peak (111) of the monoclinic phase centred at about 28.3° was used, and for ZrO$_2$, the peak (–111) of the monoclinic phase centred at 28.3 was considered.

The Williamson–Hall’s approach (WH) separates the effects of size and strain in the crystals, using the equation:

$$\beta_{\text{Total}} = \beta_{\text{Size}} + \beta_{\text{Strain}} = \frac{0.9 \cdot \lambda}{D \cdot \cos \theta} + \frac{4 \cdot (\Delta d) \cdot \sin \theta}{d \cdot \cos \theta}$$

(2)

where $\beta_{\text{Total}}$ is the full width half maximum of the XRD peak, $\lambda$ is the incident X-ray wavelength, $\theta$ is the position of the peaks, $D$ is the crystal size, and $\Delta d$ is the difference of the d spacing corresponding to a typical peak. A plot of $\beta_{\text{Total}} \cdot \cos \theta$ against $4 \cdot \sin \theta$ yields the average crystal size from the intercept value.

The BET surface areas were determined by physical adsorption of N$_2$ at −196°C in an automatic volumetric system (Autosorb-6B, Quantachrome).

Temperature Programmed Reduction with H$_2$ (H$_2$-TPR) of selected samples was carried out in a tubular quartz reactor coupled to a TCD analyser for H$_2$ consumption monitoring. The experiments were conducted with 50 mg of sample and 30 ml/min flow of 7.7 vol.% H$_2$ in Ar. The heating rate was 10°C/min. In order to quantify the total amount of H$_2$ consumed, CuO was used as calibration reference.

Catalytic tests were performed in a thermogravimetric analyser (TA Instruments, model SDT 2960) with soot:catalyst mixtures of 1:4 weight ratio. Considering that contact between soot and catalyst is a key factor in this process [9], experiments in loose and tight contact conditions were performed. For loose contact experiments, soot and catalyst were mixed with a spatula, while for tight contact tests both components were intimately mixed in a mortar. The temperature was raised at 10°C/min from 30°C until 800°C in 100 ml/min flow of air. The model soot used is a carbon black from Degussa S.A. (Printex-U), whose physico-chemical characterisation was reported elsewhere [7].

3. Results and discussion

Fig. 1 compiles the fraction of soot converted as a function of temperature for selected soot oxidation experiments. All the catalysts decreased soot oxidation temperature, and as expected, the contact between soot and catalyst drastically affects the soot oxidation process [9]. CeO$_2$ was more active than ZrO$_2$ in experiments carried out under tight contact between the soot and the catalyst. The high catalytic activity of CeO$_2$ for soot oxidation in air was attributed to the generation of highly active oxygen in the lattice due to the oxygen exchange between gas phase O$_2$ and oxygen into the oxide framework, as mentioned [4], and the redox cycle Ce$^{3+}$/Ce$^{4+}$ seems to play an important role in the oxygen exchange process. On the contrary, CeO$_2$ and ZrO$_2$ presented about the same activity in experiments...
performed in loose contact, but despite the poor contact catalyst-soot, certain catalytic activity is still observed in Fig. 1b.

Fig. 1 also compiles the soot conversion profile obtained with one of the Ce–Zr mixed oxides (Ce0.69Zr0.31O2 as a representative example). This sample reached lower soot conversion temperature than CeO2 and ZrO2, both in loose and tight contact, where the activity differences are much more important. This observation is in accordance with the results of Aneggi et al. [6] obtained with Ce–Zr mixed oxides calcined at 500 °C and aged at 750 °C in soot oxidation experiments performed in tight contact. The results presented in Fig. 1 indicate that the improved activity of Ce–Zr mixtures with regard to the bare oxides is maintained even after calcination at temperatures as high as 1000 °C.

Fig. 2 shows the parameter T50%, that represents the temperature at which 50% of soot is converted in soot oxidation experiments. The T50% temperature for non-catalysed soot oxidation is 613 °C, and CeO2 decreases this temperature to 605 and 575 °C for loose and tight contact conditions, respectively. ZrO2 shows lower activity than CeO2 in tight contact experiments (while in loose contact the differences between CeO2 and ZrO2 activity are negligible) and Ce–Zr mixed oxides present enhanced activity with regard to the pure oxides both in loose contact and tight contact conditions. The results included in Fig. 2 indicate that the Ce:Zr ratio used in the different catalysts does not affect in a great extent their activity. Aneggi et al. found an increase in the T50% parameter for CeO2 and ZrO2 catalysts if compared with the series of Ce–Zr mixed oxides calcined at the sample temperatures (750 °C); as a consequence of this, the representative curve as a function of Ce/Zr composition, assumed a volcano-type profile with a minimum in the middle composition range, characteristic of phenomena driven by the redox features of the catalyst [6]. This shape profile is similar to that found in the present work, where the five mixed oxides prepared exhibit a very improved catalytic activity with regard to the pure oxides in the tight contact experiments, being one of the intermediate compositions (Ce0.69Zr0.31O2) the best formulation prepared. A similar qualitative profile can be seen when T50% from loose contact experiments is represented. As the contact soot-catalyst is poor, the activity decreases dramatically, but the Ce–Zr mixed oxides are still better catalysts than the bare oxides, being again Ce0.69Zr0.31O2 the catalyst presenting the lowest value of T50%. This feature of Ce–Zr catalysts was not observed in La3+-doped CeO2, where an optimum La3+ loading at about 5% was observed [7].

In order to gain insight into the catalytic behaviour of Ce–Zr samples, their characterization by different techniques was carried out. Fig. 3 compiles the XRD patterns, showing that CeO2 presents the main reflections typical of a fluorite-structured material with a face centred cubic unit cell at 28.5°, 33.1°, 47.6°, 56.5°, and 59.2°, corresponding to the (111), (200), (220), (311) and (222) planes [10]. The Ce–Zr mixed oxides formed solid solutions and evidences of segregation of phases were not observed for samples Ce0.50Zr0.50O2, Ce0.70Zr0.30O2 and Ce0.69Zr0.31O2. Zr incorporation into the cubic structure of CeO2 caused the shift of peaks to lower angles, their intensity decreased and they became progressively broader, indicating less crystallinity of the oxide and smaller crystal size. The samples Ce0.59Zr0.41O2 and Ce0.49Zr0.51O2 present a small shoulder on the right side of the fluorite peak (111) that could be attributed to the coexistence of a small fraction of tetragonal phase ((111) reflection at 30°) along with the main cubic phase. In fact, phase segregation was reported in a commercial sample of Ce0.50Zr0.50O2 after calcinations at 1000 °C for 5 h [11], where the highest tendency for phase segregation is suggested by the thermodynamics [12]. A generally accepted classification of the phases in the CeO2–ZrO2 binary system assigns the t’ phase (a cation-diffusionless-formed tetragonal phase) for a Ce molar composition range between 0.30 and 0.65.

ZrO2 presents monoclinic structure, which is the stable phase predicted by thermodynamics at room temperature for pure ZrO2.

In conclusion, the phase composition of the samples prepared in this study is consistent with the phases often
observed by other authors. Although, in the intermediate composition region, the true nature of the CeO$_2$–ZrO$_2$ phase diagram is still matter of debate due to the presence of a number of stable and metastable phases of tetragonal symmetry [13].

As a summary, the phases detected in the different samples are included in Table 1 together with the crystal sizes determined with the equations of Scherrer Eq. (1) and Williamson–Hall Eq. (2). In addition, Table 1 also compiles the BET surface area of the oxides determined from the N$_2$-adsorption isotherms. These data indicate that CeO$_2$ structure collapses during calcinations at 1000 °C, and the lowest BET area and the largest average crystal size are found for this sample. Larger surface areas and smaller crystal sizes in the case of Ce–Zr mixed oxides in comparison with CeO$_2$ indicate that sintering has occurred to a larger extent in the latter, and for this reason, the Ce–Zr mixed oxides preserve a higher level of activity after calcinations at 1000 °C.

All the Ce–Zr mixed oxides present about the same BET surface area (17–19 m$^2$/g), with the only exception of Ce$_{0.89}$Zr$_{0.11}$O$_2$ that presents a slightly lower value than the others (11 against 17–18 m$^2$/g). The crystal sizes determined from the equations of Scherrer Eq. (1) and Williamson–Hall Eq. (2) are divergent. The average crystal size determined with Eq. (2) decreases monotonously from 110 nm for pure CeO$_2$ to 30 nm for pure ZrO$_2$. The crystal sizes of Ce–Zr mixed oxides ranges between 93 and 29 nm, their sizes being dependent on their Zr molar fractions. As a general trend, the crystal sizes determined from Eq. (1) also decreased as the Zr molar ratio increases. However, for ZrO$_2$, the average crystal size determined from Eq. (2) is larger than that determined from Eq. (1). In order to analyse this fact, the surface areas of the different samples were determined from the crystal sizes considering spherical symmetry, and these values are plotted in Fig. 4 as a function of the BET surface area determined from N$_2$ adsorption isotherms. An auxiliary straight line with slope = 1 has been plotted in this Figure. All the surface area values obtained with the average crystal sizes determined using Scherrer’s equation (Eq. (1)) are above the expected value, that is, they are above the auxiliary straight line, while random values lying around the auxiliary straight line are obtained by applying the Williamson–Hall’s equation. This proves that, for the samples studied, the Scherrer’s equation sub-estimates the average crystal sizes, being the equation of Williamson–Hall more convenient because separates the effects of size and strain on the crystals.

Taking into account this observation, the average crystal sizes determined from the equation of Williamson–Hall were used instead of those obtained from Scherrer’s equation. In Fig. 5, the activity of the different catalysts, represented by the $T_{50\%}$ temperature, is plotted against the average crystal size. For the set of catalysts studied, the activity does not depend on the crystal size, neither for experiments performed in loose contact between soot and catalyst nor for experiments performed in tight contact conditions. All the Ce–Zr mixed oxides present higher activity than both CeO$_2$ and ZrO$_2$ pure oxides, in spite of

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Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase/s</th>
<th>Average crystal size (nm)</th>
<th>BET (m$^2$/g)</th>
<th>Williamson–Hall</th>
<th>Scherrer</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$</td>
<td>Cubic (c)</td>
<td>110</td>
<td>57</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Ce$<em>{0.89}$Zr$</em>{0.11}$O$_2$</td>
<td>Cubic (c)</td>
<td>93</td>
<td>37</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>Ce$<em>{0.79}$Zr$</em>{0.21}$O$_2$</td>
<td>Cubic ($t''$)</td>
<td>69</td>
<td>33</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>Ce$<em>{0.69}$Zr$</em>{0.31}$O$_2$</td>
<td>Cubic ($t''$)</td>
<td>52</td>
<td>36</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>Ce$<em>{0.59}$Zr$</em>{0.41}$O$_2$</td>
<td>Cubic ($t''$)</td>
<td>39</td>
<td>18</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>Ce$<em>{0.49}$Zr$</em>{0.51}$O$_2$</td>
<td>Cubic ($t''$)</td>
<td>29</td>
<td>18</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>Monoclinic (m)</td>
<td>30</td>
<td>39</td>
<td>19</td>
<td></td>
</tr>
</tbody>
</table>

* Generally denoted $t''$. This phase does not show tetragonality of the cation sublattice and exhibits an oxygen displacement from ideal fluorite site.

** Generally denoted $t'$, being a tetragonal metastable phase.

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Fig. 4. Relationship between surface areas determined from crystal sizes (from XRD patterns) and BET surface areas (from N$_2$ adsorption isotherms at −196 °C).

Fig. 5. Catalytic activity of the different catalysts as a function of the average crystal size determined from Williamson–Hall’s equation Eq. (2).
Ce⁴⁺ and the main peak, at about 800°C, attributed to the reduction of the uppermost layers of Ce⁴⁺ to Ce³⁺, reaching the maximum consumption at high temperatures. The generally accepted argument to explain this type of profiles is that the surface and bulk reduction occur concurrently [15].

In this study, the catalytic activity of CeO₂, ZrO₂ and Ce–Zr mixed oxides for soot oxidation by O₂ has been studied with samples calcined at high temperature (1000°C). CeO₂ presents very low stability at high temperature and a low activity is exhibited after calcination at 1000°C due to sintering. 1000°C sintered-CeO₂ presented a very low surface area (2 m²/g), a large crystal size (110 nm) and a lack of surface redox properties with null surface reduction of Ce⁴⁺ by H₂ below 555°C. Zr-doping enhances significantly the thermal stability of CeO₂ and, consequently, Ce–Zr mixed oxides calcined at 1000°C are more active catalysts for soot oxidation than pure CeO₂, both in loose and tight contact with soot (mainly in the latter, as expected). Ce–Zr mixed oxides present higher BET surface areas, smaller crystal sizes and enhanced redox properties, with lower onset temperature of Ce⁴⁺ reduction by H₂, increased oxygen mobility within the lattice and a larger amount of Ce⁴⁺ that can be reduced. The Zr molar fraction does not affect in a great extent the catalytic activity of Ce–Zr mixed oxides in the range studied (Zr molar fraction from 0.11 to 0.51), and the catalytic activity of the Ce–Zr mixed oxides studied does not depend on their crystal size (crystal sizes ranging from 93 to 29 nm, respectively).

4. Conclusions

In this study, the catalytic activity of CeO₂, ZrO₂ and Ce–Zr mixed oxides for soot oxidation by O₂ has been studied with samples calcined at high temperature (1000°C). CeO₂ presents very low stability at high temperature and a low activity is exhibited after calcination at 1000°C due to sintering. 1000°C sintered-CeO₂ presented a very low surface area (2 m²/g), a large crystal size (110 nm) and a lack of surface redox properties with null surface reduction of Ce⁴⁺ by H₂ below 555°C. Zr-doping enhances significantly the thermal stability of CeO₂ and, consequently, Ce–Zr mixed oxides calcined at 1000°C are more active catalysts for soot oxidation than pure CeO₂, both in loose and tight contact with soot (mainly in the latter, as expected). Ce–Zr mixed oxides present higher BET surface areas, smaller crystal sizes and enhanced redox properties, with lower onset temperature of Ce⁴⁺ reduction by H₂, increased oxygen mobility within the lattice and a larger amount of Ce⁴⁺ that can be reduced. The Zr molar fraction does not affect in a great extent the catalytic activity of Ce–Zr mixed oxides in the range studied (Zr molar fraction from 0.11 to 0.51), and the catalytic activity of the Ce–Zr mixed oxides studied does not depend on their crystal size (crystal sizes ranging from 93 to 29 nm, respectively).

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