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Investigations into nanostructured ceria–zirconia catalysts for soot combustion

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ABSTRACT

A set of nanostructured ceria–zirconia catalysts with different Zr-contents and structural features has been prepared to study the effect of both the Zr-amount and its surface-dependent activity towards soot combustion under different experimental conditions (namely in "loose" and "tight" soot-catalyst contact). A ceria–zirconia sample has been synthesized by means of solution combustion synthesis (SCS) for comparison purposes. The physico-chemical properties of the catalysts have been investigated using complementary techniques.

The best catalytic performances have been achieved for the $Ce_{0.9}Zr_{0.1}O_2$–NP catalyst (where NP means nano-polyhedra and 0.9 indicates the atomic ratio of Ce/Ce + Zr), due to the higher mobility of the lattice oxygen within the solid, and its easier reducibility, compared to high-surface area catalysts with the same Ce/Zr ratio. Moreover, better activities, in terms of soot conversions, have been reached for $Ce_{0.9}Zr_{0.1}O_2$–NP, than similar nano-polyhedra with higher Zr-amounts (denoted as $Ce_xZr_{1-x}O_2$–NP, where $x = 0.8$ or 0.7). The substitution of some Ce^{4+} for Zr^{4+} ions favors the formation of defects (i.e., oxygen vacancies) in the ceria lattice, thus inducing a distortion of the oxygen sublattice. However, the amount of redox Ce species decreases as the Zr-content increases. It therefore seems that the incorporation of Zr^{4+} into the ceria lattice does not have a direct beneficial effect on the oxidation activity for catalysts calcined at low/mild temperatures, since it decreases the population of surface redox-active centers, which depend directly on the surface density of the Ce^{3+}–Ce^{4+} species. On the other hand, lower soot conversion values have been reached for both mesoporous ($Ce_{0.9}Zr_{0.1}O_2$–M) and microporous (50-$Ce_{0.9}Zr_{0.1}O_2$–NP/FAU) samples with the same Ce/Zr ratio. Moreover, the comparative catalyst ($Ce_{0.9}Zr_{0.1}O_2$–SCS) exhibited worse activities than the porous materials, thus confirming the key role of the textural properties for this oxidation reaction.

1. Introduction

Over the last few years, several exhaust gas after treatment technologies have been proposed to limit Diesel engine-out emissions. The latter are sources of the main outdoor air pollutants, including volatile organic compounds (VOCs), nitrogen oxides (NO_x) and particulate matter (PM), which is largely comprised of solid carbon (soot) and unburned carbonaceous compounds [1–3]. Soot, in particular, is a major constituent of air pollution, and is associated with respiratory and cardiovascular diseases as well as skin cell alterations [4]. Therefore, recent legislation has introduced more stringent PM limits for vehicles (e.g., 0.005 g/km for PM from passenger cars in Europe since 2009) and has imposed the use of catalytic technologies to satisfy the required standards [1,3]. Among the different alternatives, the entrapment of particulate from exhaust gases by Diesel particulate filters (DPFs) has received much interest in recent years [5–10]. The soot that forms Diesel exhaust particulate can be burnt off above 600 °C, whereas, typical engine exhaust temperatures fall within the 200–500 °C range [8,9]. Consequently, oxidation catalysts are required to improve the soot combustion activity within the DPFs.

According to the literature [1,3,4], ceria-based materials are among the most effective catalysts for soot combustion under either an O_2 or an NO_x/O_2 atmosphere, since they exhibit excellent redox properties of the Ce^{3+}–Ce^{4+} couple and can exchange oxygen with the gas phase. In fact, ceria alone, or doped with metals (e.g., Zr, Fe, K, La, Pr, Sm, Tb, Cu, Mn, and Mo) is able to show promising soot combustion activities [4,10–15]. The incorporation of isovalent non-reducible elements, such as Zr^{4+} ions, into a ceria lattice (Zr-content in the 20–30 mol.%) has a beneficial effect on the physico-chemical and catalytic properties of ceria, improving its thermal stability, oxygen storage capacity (OSC), oxygen mobil-

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ity in the framework, and so on [4]. Moreover, the substitution of Ce^{4+} ions with Zr^{4+} favors the formation of structural defects (e.g., terraces, ledges, kinks, and oxygen vacancies) with surface atoms having different coordination environments (namely coordination numbers, CN) [16]. It should be noted that defect sites and oxygen vacancies are among the most desirable active sites for oxidation catalysts [17,18]. In agreement with the Volkenshtein Electronic Theory [19], the presence of structural defects, associated with oxygen vacancies, in fact modifies the Fermi Energy level, thus, favoring oxidation reactions [20]. Therefore, it can be expected that ceria–zirconia catalysts will exhibit superior soot oxidation activities than pure ceria [4,10–15].

However, it should be pointed out that the feasibility of the soot combustion mechanism depends to a great extent on the soot-catalyst contact points, and hence it is necessary to maximize the interaction between the soot particles and the catalyst surface [11,14].

Over the last few decades, many studies related to CeO_2 nanoparticles have shown that surface atoms with a lower CN usually exhibit higher chemical reactivity, and are therefore, the preferred active centers for catalytic reactions [1,10]. Nanomaterials are notable because of their small featured size, which endows them with structure-dependent properties, due to the high surface-to-volume ratio (the small size maximizes the surface active sites) and unique electronic features (=discrete behavior) [18–20].

However, the reactivity of nanoparticles depends not only on their size, but also on the crystal surfaces and thus, on the exposed planes [21,22]. Nanostructured CeO_2-based materials, having specific surface planes, have shown promising catalytic activities for many reactions, including soot combustion [10,23–31]. Small ceria particles, with an abundance of (1 0 0) and (1 10) planes, are usually more active than larger CeO_2-particles with preferred exposure of the (1 1 1) planes [32–34]. A study by Zhang et al. [35] on ceria nanocubes, that exposed six (1 0 0) surfaces, revealed greater oxygen storage which can be attributed to the ease of O extraction from those surfaces. On the other hand, since the overall oxidation activity depends on the surface area available from the solid catalyst, it is necessary to maximize the dispersion of the nanoparticles using high-surface-area supports, such as zeolites [1,9].

In the present work, a set of ceria–zirconia catalysts, with different Zr-contents and structural properties, has been prepared to investigate the effect of both Zr-loading and the surface-dependency activity of catalysts towards the soot oxidation reaction. The physico-chemical properties of the prepared materials have also been studied using complementary techniques.

2. Experimental

2.1. Preparation of the samples

Three nanostructured ceria–zirconia catalysts (denoted hereafter as $Ce_xZr_{1-x}O_2$–NP where NP means nano-polyhedra, whereas x = 0.9, 0.8, or 0.7 indicates the atomic ratio of Ce/Ce + Zr) have been synthesized by means of a hydrothermal procedure. During a typical synthesis, appropriate amounts of $Ce(NO_3)_3{\cdot}6H_2O$ and $ZrOCl_2{\cdot}8H_2O$ (Sigma–Aldrich) were dissolved in 30 mL of distilled water ("solution I"). Zirconyl chloride was chosen as Zr precursor, since it is a proper candidate for the synthesis of the ceria–zirconia nanostructures by hydrothermal procedure [36]. Meanwhile, "solution II" was prepared by adding NaOH (24 g) to distilled water (35 mL). The two solutions were then mixed together and stirred at room temperature for 1 h, which resulted in the formation of a milky slurry. The final mixture was transferred to a Teflon autoclave (150 mL) which was 70% filled with deionized water. The mixture was then aged at 110 °C for 24 h. The fresh precipitates were separated by centrifugation, washed with deionized water and ethanol several times and dried at 90 °C overnight. The powders were calcined at 550 °C for 4 h.

An ordered mesoporous sample (denoted as $Ce_{0.9}Zr_{0.1}O_2$–M) was prepared by means of the following procedure: 0.35 g of $Ce(NO_3)_3{\cdot}6H_2O$ and 0.05 g of $ZrO(NO_3)_2$ (Sigma–Aldrich) were dissolved in 5 mL of absolute ethanol. Then, 0.15 g of KIT-6 (mesoporous silica molecular sieve by ACS materials) was added to this solution and heated at 60 °C under vigorous stirring for 30 min. After the ethanol had evaporated, the cerium precursor/silica composite was calcined at 350 °C for 4 h. The impregnation step was repeated in order to achieve higher loadings. The powder was dried at 110 °C overnight and calcined at 550 °C for 6 h. The silica template was then removed and treated three times with a 2 M NaOH solution at 50 °C (10 min each time). The powder was washed with deionized water. Finally, the obtained product was dried at 90 °C overnight.

The 25-, 50-, and 75-$Ce_{0.9}Zr_{0.1}O_2$–NP/FAU catalysts ($Ce_{0.9}Zr_{0.1}O_2$–NP contents = 25, 50, and 75 wt.%, respectively) were prepared by adding appropriate amounts of $Ce_{0.9}Zr_{0.1}O_2$–NP to the Faujasite-type zeolite (Sigma–Aldrich), and placing the mixtures in a rotary evaporator at 60 °C to evacuate the water. The obtained solids were then dried at 90 °C overnight. A ceria–zirconia sample (denoted as $Ce_{0.9}Zr_{0.1}O_2$–SCS) was prepared by means of solution combustion synthesis (SCS) for comparison purposes [37]. In short, a homogeneous aqueous solution of $Ce(NO_3)_3{\cdot}6H_2O$ (1.9 g), $ZrO(NO_3)_2$ (0.11 g) and urea (0.8 g), prepared at room temperature, was placed in an oven at 600 °C for 20 min. The resultant powder was washed with deionized water to remove impurities and then dried at 90 °C overnight.

2.2. Characterization of the catalysts

The powder X-ray diffraction patterns have been collected on a X'Pert Philips PW3040 diffractometer using Cu Kα radiation (2θ range = 20–70°; step = 0.05° 2θ; time per step = 0.2 s). The diffraction peaks were indexed according to the Powder Data File database (PDF 2000, International Center of Diffraction Data, Pennsylvania). The average size of the crystallites was obtained using the Scherrer formula, $D = 0.9\,\lambda/b\cos\theta$, where λ is the wavelength of the Cu Kα radiation, b is the full width at half maximum (in radians), 0.9 is the shape factor for spherical particles, and θ is the angle of the diffraction peaks.

The Specific Surface Area (S_{BET}), total pore volume (V_p), and average pore diameter (D_p) were measured by means of N_2 physisorption at −196 °C (Micrometrics ASAP 2020) on samples previously outgassed at 200 °C for 4 h to remove water and other atmospheric contaminants. The specific surface area of the samples was calculated using the BET method, whereas the pore diameters were evaluated by applying the Barrett–Joyner–Halenda (BJH) algorithm to the isotherm desorption branch.

Sample morphology was studied by using a field emission scanning electron microscope (FESEM Zeiss MERLIN, Gemini-II column) and Transmission Electron Microscopy (TEM, Jeol JEM 3010 operating at 200 kV). The Ce/Zr-content in the samples was determined through EDS analysis (Oxford X-ACT): 5 different spots with a 10–50 nm diameter were selected in representative zones of the sample, and the average Ce/Zr-content was then calculated.

H_2-TPR analysis was carried out in a Thermoquest TPD/R/O 1100 analyzer equipped with a thermal conductibility (TCD) detector: a 50 mg sample was placed in a quartz tube, then put in contact with reducing flowing gas (4.95% molar H_2 in Ar, 40 $cm^3\,min^{-1}$) and heated in the 25–900 °C temperature range (heating rate: 5 °C min^{-1}), while H_2 consumption was recorded using a thermal conductivity detector (TCD).