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Nanostructured ceria-based catalysts for soot combustion: Investigations on the surface sensitivity

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ABSTRACT

A set of ceria nanomaterials with different topological and textural properties has been prepared to investigate the shape-dependency activity of ceria towards soot combustion under different reaction conditions (namely in "loose" and "tight" contact). The physico-chemical properties of the prepared catalysts have been studied using complementary techniques. The best performances, in terms of the total oxidation of soot, have been achieved for the CeO_2-nanocubes, due to the abundance of coordinative unsaturated atomic sites on the (1 0 0) and (1 1 0) exposed surfaces (namely truncated nanocubes). However, better results, in terms of the onset of soot oxidation, have been obtained for high-surface-area materials, thus reflecting the key role of surface area at low temperatures. Activity tests have suggested the surface-sensitivity of soot oxidation over the prepared ceria-based materials, when the reaction temperature was above 410 °C or 370 °C (in "loose" or "tight" conditions, respectively). On the other hand, the reaction has appeared surface-insensitive at a lower temperature. Hence, soot oxidation over these ceria compounds can be considered a reaction that displays both surface-sensitive and surface-insensitive behaviour, which depend on the experimental conditions.

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1. Introduction

Diesel and gasoline engines are sources of the main outdoor air pollutants, such as volatile organic compounds (VOCs), NO_x and particulate matter (PM), whose reduction represents a very challenging task [1–3]. Diesel particulate emissions are suspected of causing several health problems, including lung cancer, and hence research into soot abatement in the exhaust of diesel engines has received much interest over the last few years [4–7]. Recent legislation has introduced more stringent NO_x and particulate limits for light and heavy-duty vehicles as well as for passenger cars, and has imposed the use of catalytic devices to satisfy the required standards [1,3,7].

The solid carbon (soot) that forms diesel exhaust particulates can be burnt off above 600 °C, although typical diesel engine exhaust temperatures fall within the 200–500 °C range [7,8]. Therefore, oxidation catalysts can be used to increase the oxidation rate of filter traps at lower temperatures. Ceria-based materials are among the most active soot oxidation catalysts under either O_2 or in a NO_x/O_2 atmosphere. Ceria alone, or in combination with other metal oxides, may exhibit promising soot oxidation activity [1,4,9–14]. The redox behaviour, as well as the availability of chemisorbed oxygens (α-species), are the most important factors that play a role on the oxidation activity of CeO_2-based materials [15–19]. However, the number of soot-catalyst contact points also affects the catalytic activity of ceria for soot oxidation and it is therefore necessary to maximize the interaction between the soot particles and the catalyst surface [10,13].

Over the last few decades, there has been significant progress in the nanoscale controlled synthesis of CeO_2-based materials for a number of catalytic applications. Different shapes and sizes of ceria have been synthesized using methods designed by many research groups [20]. In general, nanostructured materials are notable because of their small featured size, which endows them with size- and shape-dependent properties due to the high surface-to-volume ratio (=higher number of coordinatively unsaturated sites), and their unique electronic features (quantum size effects) [21–26]. Hence, the catalytic activity of nanomaterials depends not only on the crystal size, but also on the crystal surfaces and thus on the exposed planes [27–29]. The higher chemical reactivity of specific ceria surfaces has been confirmed in a number of reactions, such as CO oxidation, CO_2 reforming of methane, methanol and ethanol reforming and low-temperature WGS and, more recently, soot oxidation [30–37].

Ceria nanomaterials with well-defined reactive (1 0 0) and (1 1 0) planes are usually more active than conventional

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polycrystalline ceria NPs with preferred exposure of (1 1 1) planes [38]. Data reported for several catalytic reactions suggest that the order of chemical reactivity for CeO_2-nanostructures is nanocubes > nanorods > polycrystalline ceria NPs [38,39]. This sequence reflects the reverse order of the surface stability of ceria: (1 0 0) and (1 1 0) < (1 1 1) facets [38–41]. However, it has been observed, for both CO and soot oxidation, that the thermal treatment of polycrystalline ceria at $T > 500\,^{\circ}C$ promotes the exposure of more reactive surfaces, such as (1 0 0) and (1 1 0) facets, whereas it progressively reduces exposure of less reactive surfaces, such as (1 1 1) planes [9].

However, the beneficial role of the textural properties (e.g. specific surface area, total pore volume, pore diameter and so on) on the overall catalytic activity of CeO_2 for various reactions, including soot combustion, is well known [1,9]. Therefore, it is necessary to maximize the exposure of more reactive surfaces of CeO_2 using high surface area materials as supports.

In the present work, a set of CeO_2 samples with different topological and textural properties (CeO_2-nanocubes, CeO_2-nanocubes over ZSM-5-type zeolite, CeO_2-nanorods, mesoporous CeO_2 and CeO_2-SCS) has been prepared to investigate the shape-dependency activity of ceria towards soot combustion under different reaction conditions (namely in "loose" and "tight" contact). The physicochemical properties of the prepared catalysts were studied using complementary techniques.

2. Experimental

2.1. Preparation of the samples

CeO_2-nanorods and CeO_2-nanocubes (denoted hereafter as Ce-NR and Ce-NC, respectively) have been synthesized through the hydrothermal procedure [42,43]. During a typical synthesis, appropriate amounts of NaOH (24 g) and $Ce(NO_3)_3{\cdot}6H_2O$ (2.2 g) (Sigma–Aldrich) were dissolved in 35 mL and 5 mL of bi-distilled water, respectively. The two solutions were then mixed together and stirred for 1 h, which resulted in the formation of a milky slurry. The final mixture was transferred to an autoclave (150 mL) which was 75% filled with deionised water. The mixture was then aged at either 100 °C (to form nanorods) or at 165 °C (to form nanocubes) for 24 h. The fresh precipitates were then separated by centrifugation, washed with deionised water several times, washed in ethanol and dried at 60 °C overnight. The powders were calcined at 550 °C in synthetic air for 4 h.

The synthesis of the mesoporous ceria (denoted as Ce-M) was [42]: 2.5 g of $Ce(NO_3)_3{\cdot}6H_2O$ (Sigma–Aldrich) was dissolved in 20 mL of absolute ethanol. 0.5 g SBA-15 (ACS materials) was added to this solution and heated at 60 °C under vigorous stirring. After the ethanol had evaporated, the cerium precursor/silica composite was calcined at 450 °C for 4 h. The procedure was repeated once more with an ethanol solution of 1.2 g $Ce(NO_3)_3{\cdot}6H_2O$. The powder was dried at 110 °C overnight and calcined at 550 °C in synthetic air for 4 h. The silica template was then removed and treated three times with 2 M NaOH solution at 50 °C (10 min each time). Finally, the obtained product was dried at 60 °C overnight.

The Ce-NC/ZSM-5 sample was prepared by adding an appropriate amount of Ce-NC solution to the ZSM-5 type zeolite (Zeolyst International) and placing the mixture in a rotary evaporator at 60 °C in order to progressively evacuate the water. The obtained solid (CeO_2/ZSM-5 = 1.0 by weight) was then dried at 90 °C overnight.

A comparative mesoporous sample (denoted as Ce-SCS) was prepared by solution combustion synthesis (SCS) [2,45]. In short, a homogeneous aqueous solution of $Ce(NO_3)_3{\cdot}6H_2O$ (1.9 g) (Sigma–Aldrich) 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 deionised water to remove impurities and then dried 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 Centre of Diffraction Data, Pennsylvania). The average size of the crystallites was determined 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.

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, and the pore diameters were evaluated by applying the Barrett–Joyner–Halenda (BJH) algorithm to the isotherm desorption branch.

Sample morphology was investigated by means of 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 Si-content in the Ce-M sample was determined through EDS analysis (Oxford X-ACT): three different spots with a 10–50 nm diameter were selected in representative zones of the sample, and the average Si-content was then calculated.

For H_2-TPR measurements, 50 mg catalyst was pre-treated under air flow (40 $cm^3\,min^{-1}$) at 150 °C for 1 h, to remove water and other atmospheric contaminants, and subsequently cooled to 25 °C with Ar. TPR analysis was carried out by heating the sample up to 950 °C at a constant rate of 5 °C min^{-1} under an Ar flow (4.95% molar H_2 in Ar). H_2 consumption was recorded using a thermal conductivity detector (TCD).

XPS (X-ray photoelectron spectroscopy) measurements were obtained on XPS PHI 5000 Versa probe apparatus using a band-pass energy of 187.85 eV, a 45° take off angle and a 100.0 μm diameter X-ray spot size. Curve-fits were performed by means of Multipack 9.0 software.

2.3. Catalytic activity tests

The soot oxidation activity of the catalysts has been measured by means of temperature programmed oxidation (TPO), which was carried out in a fixed-bed micro-reactor (a quartz U-tube, with an inner diameter of 4 mm, heated by an electric furnace). The temperature was measured by a thermocouple placed close to the middle of the catalytic bed. An N_2 flow, containing 10% of O_2, was fed at a constant rate of 100 $cm^3\,min^{-1}$, to the fixed bed, which was constituted by 50 mg of a carbon mixture (Printex-U) and powdered catalyst (=45 mg of catalyst and 5 mg of soot) mixed with 150 mg of inert silica. Two types of contact conditions were considered:

- "*Loose*" *contact*: the catalyst–soot mixture was prepared by gently shaking it with a spatula in a polyethylene vessel for 1 min. This procedure was sufficient to homogenize the mixture, but still allowed the two solid phases to be loosely put in contact. Although the procedure was very short, the established contact led to a reproducible catalytic performance;
- "*Tight*" *contact*: the catalyst–soot mixture was obtained through a 10 min ball milling at 250 rpm (IG/W2/E, Giuliani Tecnologie) to reach a close contact between the catalyst and soot. This

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