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Experimental evidences of the relationship between reducibility and micro- and nanostructure in commercial high surface area ceria

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ABSTRACT

Two commercial high BET surface areas CeO_2 are characterized, as received and after calcination at different temperatures, to better understand the relationship between reducibility and micro- and nanostructure. Combination of TPR data, Rietveld analysis of XRD diagrams and HREM/HAADF-STEM suggest that the nano-particles are responsible for Ce^{4+} reduction in the moderate temperature range. Results obtained in this work show that previous models based on kinetic and theoretical analysis can be fully supported by morphological characterization. This study unveils the key parameters that must be known in order to select appropriate commercial ceria samples.

1. Introduction

From the pioneer use in three-way catalysts for automotive pollution control till the most recent application in hydrogen production reactions for fuel cell technology, the attractive redox properties of CeO_2 has captured the attention of scientists [1,2]. The literature on these topics is so vast that it is really amazing how still today there is some controversy in the interpretation of ceria redox behaviour, in particular the origin of the two reducibility thermal regions that a high surface area ceria uses to present. Classically reduction at low and high temperature have been associated to surface and bulk reduction respectively [3], the former based on a linear relationship between the peak area and surface area, which was used to estimate the surface area of mixed materials [4]. On the contrary, other authors [5–7] have suggested differences in the intrinsic thermodynamic properties of ceria particles as a function of their size as responsible for the appearance of two distinctive reduction events.

Certainly, in the last 20 years an extraordinary progress has been made in the enhancement of ceria redox performance by appropriate doping, mainly with zirconia [8–11] and other rare earth oxides [12–16]. It is also remarkable the great step forward achieved in the synthesis and characterization of ceria nanocrystals with controlled morphology, structure and defect concentration, which is of significance for ceria-catalyzed oxidation reactions [17–21]. Recently there has been a lot of research aiming at the relation between the nanostructure and the reducibility of ceria [22], in particular theoretical studies [23]. Taking into account the use of H_2 as conventional molecule probe for this kind of studies, numerous theoretical investigations of both bulk and surface reduction of CeO_2 have been also reported, paying special attention to the interactions of atomic H with CeO_2 (1 1 1) and (1 1 0) surfaces [24]. Therefore it is very surprising that a similarly rigorous analysis is missing when dealing with commercial ceria powders widely employed. Although the importance of micro- and mesoporosity in determining the textural stability of CeO_2 based materials has been previously discussed [9], it is still often assumed that any high surface area ceria sample will deliver good redox performance for catalytic applications and will behave in a similar way. This is so as scarce information about the thermal and chemical history of the raw materials is usually provided by the suppliers. Thus, the novelty of this work is to evaluate the validity of such assumption on the basis of experimental data. In particular, it aims at gaining a better understanding about the influence of additional parameters, other than the BET specific surface area, on the reducibility of ceria, as the latter is a key property in the catalytic reactions for which this material is usually employed [1–3,5,6].

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2. Experimental

2.1. Materials

In this work two different ceria provided by the same manufacturer, Rhodia (previously Rhône Poulenc) have been investigated. The samples were supplied at different times, 2001 and 2009, as a highly pure (≥99.5%) fine powder (5–15 μm), just labelled as high surface area cerium oxides without any additional information, except their respective batch numbers, 96067/01 and 03535201AC0. Selection of these samples was made as representative of the evolution on the characteristics of the same product from a worldwide leading company, well-known in the rare earth oxides market. In order to investigate their thermal stability, both starting materials were submitted to a heating treatment under static air for 2 h at 500, 700 and 900 °C. Hereafter the starting, or fresh, samples will be referred to by the name CeO_2 followed by the roman numerals I and II, in correspondence with the order of their delivery. In the case of the calcined samples a second decimal digit (5, 7 or 9) will be added to the name as a way to refer to the calcination treatment used to prepare them. These numbers correspond to the first digit of the maximum temperature reached during calcination.

2.2. Characterization techniques

Textural characterization of the samples was carried out by measuring the adsorption/desorption of N_2 at −196 °C, employing a Micromeritics ASAP 2020 device. The experiments were performed using 250 mg of sample. Before the measurement, all the samples were submitted to a surface cleaning pre-treatment under high vacuum at (unless indicated) 200 °C for 2 h. The obtained isotherms were used to calculate the specific surface area (S_{BET}) as well as the micro- and meso-porosity features of the studied samples.

Reducibility of the samples in dynamic H_2 atmosphere was examined by means of Temperature-Programmed Reduction (TPR) experiments performed in a TA Instruments thermobalance, SDT Q600 model, working with 80–110 mg of sample. In all cases a 60 cm^3 min^{-1} flow of H_2 (3%)/Ar was used, heating in a linear program at a rate of 10 °C min^{-1} from room temperature up to 900 °C. To ensure starting from a total oxidised state and a clean surface, prior to each experiment the sample was pretreated with O_2 (5%)/He (60 cm^3 min^{-1}) at 500 °C for 1 h and further cooling down to 150 °C under the same atmosphere before switching to helium. The details of this pre-treatment were selected according to previous Temperature-Programmed Oxidation (TPO) experiments (not shown) aimed at defining the temperature necessary to remove any species that could further interfere in the calculation of the percentage of reduction from the weight losses recorded during the TPR study.

Induced Coupled Plasma spectroscopy (ICP) analysis of the chemical composition was performed using an IRIS Intrepid HR instrument. Also X-ray Fluorescence (XRF) analysis in a Bruker S4 Pioneer spectrometer was carried out for the same purpose.

X-ray diffractograms (XRD) were obtained in a BRUKER D8 ADVANCE 500 powder diffractometer using Cu Kα radiation (40 kV, 40 mA). The diagrams were recorded in the 2θ angle range from 2° to 132°, using a step size of 0.03° and a counting time of 40 s. For a Rietveld refined estimate of the lattice parameter and crystal size, the BGMN software from Joerg Bergmann was used [25].

The granulometric study was carried out using a Mastersizer 2000 granulometer from Malvern Instrument, operating with laser diffraction. Typically, 100 mg of solid were dispersed in 20 ml of water and 1 ml of acetic acid. A few drops of the solution prepared were added to the sample chamber until getting 10% of obscuration. To ensure reproducibility of the measurements, results were obtained in each case as the average of three independent runs.

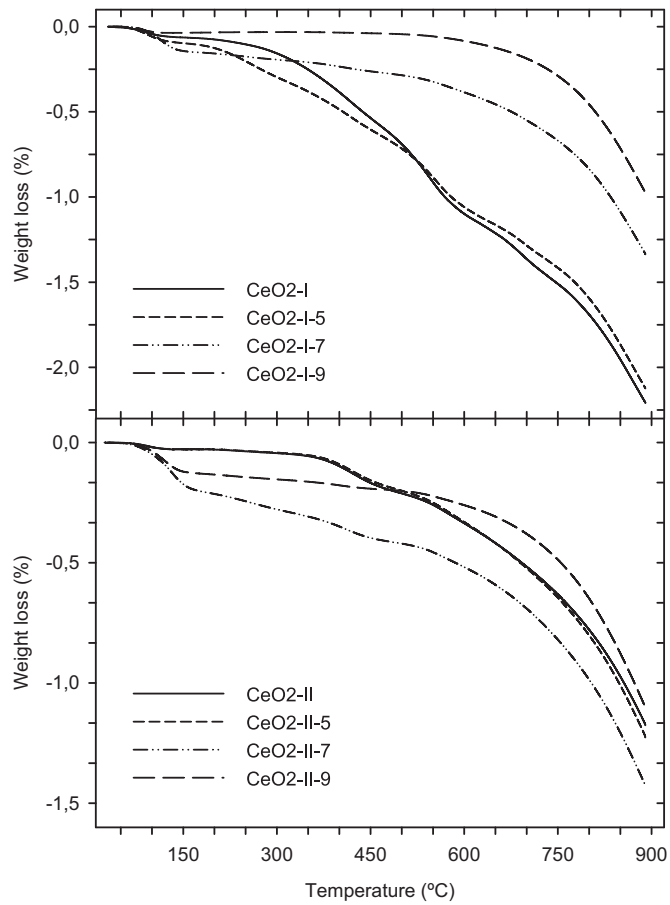

Fig. 1. Thermogravimetric curves obtained by heating at 10 °C min^{-1} under a 60 cm^3 min^{-1} flow of H_2 (3%)/Ar.

Secondary Electron Scanning Electron Microscopy (SEM) images, with nominal resolution about 3 nm, were obtained in a QUANTA-200 Scanning Electron Microscope.

Transmission electron microscopy studies were performed with a JEOL2010F microscope, working at 200 kV. This instrument had a structural resolution of 0.19 nm, and it was equipped with a high angle-annular dark field detector for scanning transmission electron microscopy (HAADF-STEM) technique. Electron diffraction patterns were acquired using a 120 cm camera length.

3. Results and discussion

3.1. Reducibility

Fig. 1 shows the thermogravimetric traces related to the irreversible reduction process in dynamic 3%-H_2 atmosphere of the two ceria samples investigated after the oxidizing pre-treatment described in Section 2. Preliminary studies (Fig. S1 of Supplementary Information) allowed discarding the presence of residual carbonates after such pre-treatment so ensuring that only oxygen elimination with water production is taking place in these experiments [26]. To facilitate the analysis, percentage of ceria reduction was estimated from the weight losses, their corresponding derivative traces being shown in Fig. 2. Derivative curves obtained for both fresh oxides (not represented) were similar to those obtained in each case after calcination at 500 °C. In all plots depicted the well reported peak of ceria reduction at high temperature (approx. 900 °C) is observed. Nevertheless, the relevant result in this study is that comparison between CeO_2-I-5 and CeO_2-II-5 reveals that the former exhibit more intense peaks at 250 and 550 °C. Moreover,