

IR investigation of the interaction of deuterium with $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ and Cl-doped $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$

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Abstract

The interaction of deuterium with $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$, synthesised by a co-precipitation technique, is discussed on the basis of the sample's bulk and surface composition and the presence of trace amounts of silicon. Redox cycling resulted in surface cerium enrichment, which, however, only moderately affected the interaction of the material with D_2 . Addition of a trace amount of chloride ion to the oxide surface promoted both H/D scrambling and vacancy creation. Chloride ion was also found to prevent the surface cerium enrichment induced by redox cycling.

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1. Introduction

Ceria–zirconia (CZ) mixed oxides represent today's most advanced additives to enlarge the operating air-to-fuel window of a three-way catalyst [1]. This particular ability consists in storing and releasing bulk oxygen via the $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox couple (the Oxygen Storage Capacity, OSC). At the same time, these materials can contribute to stabilise noble metal dispersion [2,3] and promote the water gas shift and reforming reactions [4,5]. More recently, CZ mixed oxides have attracted attention as promising catalyst supports for the production and purification of hydrogen [6–9]. The high oxygen mobility of these materials is believed to be responsible for their superior activity with respect to traditional supports, lattice oxygen being involved in catalytic reactions.

In view of their widespread use as a catalytic support, the redox properties of CZ mixed oxides have been extensively and systematically studied. Attempts to rationalize the unusual redox behaviour of these materials have generally focused either on variation in bulk structure [10–12] or in surface properties [13–15] to explain their properties. However, to date a clear picture has not emerged. In the present work, we

investigate the redox behaviour of $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$, in conjunction with both bulk and surface characterization techniques, in order to identify surface or bulk properties, which may be critical in the overall behaviour observed. In this context, the effect of chloride ion incorporation on the redox behaviour was also investigated. Interest in the use of chloride ion as a dopant is many-fold: (i) it offers a simple way to introduce surface modification, either through its interaction with hydroxyl groups to form oxychloride species [16] or by adsorption on cationic sites [17]; (ii) chloride ions very often poison catalytic processes, even when present from the synthesis stage [18]; (iii) in the specific case of redox behaviour, chloride ions can strongly affect the phenomenon of spillover when a metal is present [19]; (iv) previous reports have indicated that high temperature reaction between CZ mixed oxides and chloride ion supported thereon, a process described as chemical filing, promotes low temperature reduction of the mixed oxides [20,21].

2. Experimental methods

$\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ was prepared by a co-precipitation technique, as described below. To an aqueous solution of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Aldrich 99.9%), an excess of ammonium peroxodisulphate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) (Carlo Erba 97%) was added, in order to oxidise the cerium ions [22]. The solution was stirred vigorously at

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the boiling point (30 min) to ensure complete cerium oxidation and decomposition of the excess peroxodisulphate. After addition of an aqueous solution of $ZrO(NO_3)_2 \cdot xH_2O$ (Aldrich 99.9%) at room temperature (rt), sodium hydroxide solution (15 wt.%) was added under stirring until the pH reached a value of 13, then stirring was continued for 1 h. The product was filtered, washed with water, suspended in water, stirred for 30 min and filtered again. This process was repeated until the Na^+ concentration in the mother liquor was less than 10 ppm. After the final washing, the sample was dried overnight (383 K), then calcined in air for 5 h at 773 K ($3 K min^{-1}$). This material is hereafter referred to as CZ60.

Chloride ion was loaded onto CZ60 by incipient wetness impregnation with a solution of NH_4Cl , the concentration of which was adjusted to obtain a chloride ion loading of 0.03 (w/w). The sample thus impregnated was dried at 383 K overnight. In the following text, the notation CZ60(Cl) is used to indicate the nominal Cl loading of the sample. The value of 0.03% chloride correspond, to ca. 1% of the surface cations present, assuming that the (1 0 0) or an equivalent face of an fcc unit cell ($a = 0.53 nm$) is exposed.

N_2 adsorption isotherms at 77 K were obtained on a Micromeritics ASAP 2000 analyzer, after degassing the sample at 623 K for 12 h.

Powder X-ray diffraction patterns were collected on a Siemens Kristalloflex Mod.F Instrument (Ni-filtered $Cu K\alpha$). A simplified fitting procedure, using the PowderCell 2.4 program, was employed to estimate phase composition.

In-situ FT-IR spectra were collected at rt on a Perkin Elmer 2000 FT-IR spectrometer with MCT detector using a static quartz cell. For analysis, the powdered samples were pressed into self-supporting discs. A cleaning/activation procedure, consisting of calcination with oxygen at 773 K (300 mbar, 1 h) followed by evacuation at 773 K (1 h), was employed as a standard first step in all investigations. Reduction studies were performed by exposing the sample to 150 mbar of D_2 at rt, followed by: (1) heating for 0.5 h at the selected temperature (up to 773 K); (2) cooling to rt under D_2 to record the spectra; (3) heating to the selected temperature, evacuation for 0.5 h, then cooling to rt to record the spectra. Methanol adsorption studies were conducted by exposure of the cleaned samples to methanol vapour (25 mbar, rt for 10 min) followed by evacuation. After recording the spectrum, the sample was heated for 1 h at 373 K under vacuum, then, cooled to collect the spectra. During all these treatments, the vacuum reached after 1 h of pumping under dynamic conditions was of the order of 1×10^{-8} mbar, while the residual vacuum under static conditions was of the order of 1×10^{-7} mbar.

Fluorescence spectra were collected on a Philips 1400 instrument.

TPR experiments were performed using a VG Sensorlab quadrupole mass spectrometer. Typically, 0.2 g of sample were employed, in U-shaped quartz reactors and supported on quartz granules. An additional layer of quartz was added on top to ensure thermal homogeneity of the gas passing over the sample. The outlet of the reactor was connected via a heated capillary tube to the mass spectrometer. Analysis was performed under 5%

D_2/Ar (flow rate = $25 ml min^{-1}$) and up to 1173 K ($10 K min^{-1}$), at which temperature the samples were reduced isothermally for 15 min. H_2 was then passed over the sample (5% in Ar, 60 min) to restore surface OH groups. After TPR, the samples were outgassed under Ar flow at 1173 K for 15 min and cooled to 700 K, at which temperature oxidation was carried out in flowing 5% O_2 in Ar. This ensures full oxidation in the bulk of the solid solution. The TPR/oxidation procedure was typically repeated four times, to investigate the effects of such cycling on the redox properties of the samples. The reoxidation step of the third cycle was conducted at 973 K in order to evaluate the effect of more severe oxidation conditions. The total oxygen storage capacity (OSC) was measured in a separate set of experiments with a Micromeritics TPD/TPR 2900 apparatus. After TPR, the samples were oxidised at 700 K with pulses of O_2 (loop 0.1 ml).

3. Results and discussion

3.1. Textural and structural characterization of CZ60

N_2 adsorption at 77 K indicated a mesoporous material with a BET surface area of $115 m^2 g^{-1}$, a BJH average pore diameter of 17 nm (as calculated from the desorption isotherm) and a total pore volume of $0.62 ml g^{-1}$. Upon calcination at 1273 K, the surface area and the pore volume decrease strongly (BET $< 10 m^2 g^{-1}$; total pore volume $0.02 ml g^{-1}$). TPR to 1173 K followed by reoxidation at 700 K results in a similar, although less severe, textural modification (BET $30 m^2 g^{-1}$, total pore volume $0.37 ml g^{-1}$, average pore diameter of 44 nm).

XRD analysis of CZ60 (i.e., after calcination at 773 K) indicated a poorly crystalline material. Due to the consequent broadness of the peaks, it was not possible to determine structural data. Fig. 1 reports the XRD patterns obtained after calcination at 1073 and 1273 K, as well as that after TPR to 1173 K followed by reoxidation at 700 K. All of the features observed are clearly composed of unresolved peaks, thereby, indicating compositional inhomogeneity in the samples. As outlined in Table 1, in all cases good fits of the experimental data were obtained by assuming the presence of two phases: a predominant tetragonal phase and a cerium-rich cubic phase. Of the three treatments, TPR/reoxidation results in the most

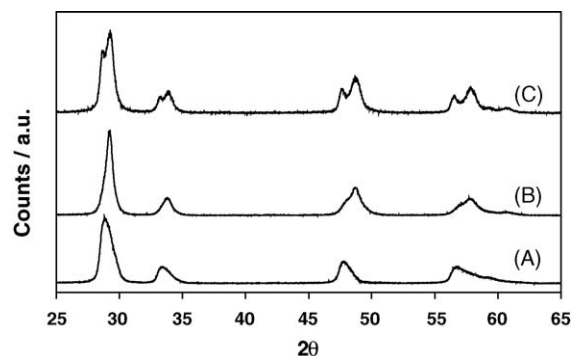


Fig. 1. XRD patterns of CZ60: (A) after calcination at 1073 K, (B) after calcination at 1273 K and (C) after temperature programmed reduction to 1173 K and oxidation at 700 K.

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