



## Feature Article

# Improving the ceria-mediated water and carbon dioxide splitting through the addition of chromium



Sotiria Mostrou<sup>a,b</sup>, Robert Büchel<sup>a,\*</sup>, Sotiris E. Pratsinis<sup>a</sup>, Jeroen A. van Bokhoven<sup>b,c,\*\*</sup>

<sup>a</sup> Particle Technology Laboratory, Department of Mechanical and Process Engineering, ETH Zurich, Sonneggstrasse 3, 8092 Zurich, Switzerland

<sup>b</sup> Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, Vladimir-Prelog-Weg 1, 8093 Zurich, Switzerland

<sup>c</sup> Laboratory for Catalysis and Sustainable Chemistry, Paul Scherrer Institute, WLG 135, 5232 Villigen, Switzerland

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## ABSTRACT

The solar thermochemical water and carbon dioxide splitting, mediated by ceria, has a great potential to produce “green” syngas. Chromium was added to ceria to improve the syngas production. Three preparation methods were applied, resulting in different morphologies allowing to investigate the role of chromium. The samples were characterized by X-ray diffraction, Raman and X-ray spectroscopy, and electron microscopy. Materials made by polymerized-complex-method and dry-impregnation consisted of two crystal phases: ceria and chromia. In contrast, materials made by flame-spray pyrolysis exhibited a homogeneous Cr-doped ceria phase, and chromia was found only at a chromium-content higher than 25 mol%. The chromium-doped ceria released additional oxygen during the formation of CeCrO<sub>3</sub> perovskite, which did not enhance hydrogen or carbon monoxide production. All chromia-containing samples exhibited improved oxygen exchange capacity, possibly due to a redox cycle of chromia itself, and significantly improved the activity of water and carbon dioxide splitting. Hydrogen production increased from 3.2 to 6.7 mL/g and the time to reach redox equilibrium was shortened from 41 to 3 min. The best hydrogen and carbon dioxide production rates were up to 20 and 500 times higher than pure ceria, respectively. The presence of chromium is therefore crucial as a catalyst, promoter, and oxygen storage enhancer. This work emphasises the importance of a catalysed re-oxidation reaction and demonstrates that a metal oxide, becoming active *in situ*, can catalyse water and carbon dioxide splitting.

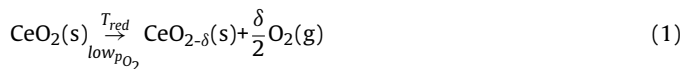
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## 1. Introduction

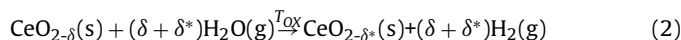
Liquid fuels, from fossil-free sources, are very important in the attempt to meet the increasing energy demands, while restraining emissions of anthropogenic carbon dioxide [1]. Solar thermochemical water splitting (WS) and carbon dioxide splitting (CDS) utilize solar radiation [2] to produce hydrogen and carbon monoxide from carbon dioxide and water [3,4]. The produced hydrogen can be used as fuel without further treatment, or together with carbon monoxide (syngas) to yield liquid solar fuels and other chemicals via Fischer-Tropsch synthesis [5]. The WS and CDS reactions are realized by means of a reduction-oxidation (redox) cycle of materials with a high oxygen exchange capacity, such as ceria. The latter was used for WS and CDS, separately [6,7] or simulta-

neously [8]. The WS and CDS mechanisms are similar, in that they include a redox cycle as shown in Eqs. (1)–(3). The reduction step (Eq. (1)) is an exothermic reduction of ceria at low oxygen partial pressure and high temperature; between 750–1500 °C, the non-stoichiometry  $\delta$  is in the region of 0.001–0.3 [9]. Above 2000 °C, ceria reduces stoichiometric to Ce<sub>2</sub>O<sub>3</sub> [6]. After the reduction step, ceria is cooled and reacts with water and carbon dioxide (Eqs. (2) and (3)) to produce hydrogen and carbon monoxide, respectively. The re-oxidation potential depends on the non-stoichiometry, and it is thermodynamically favourable below 927 °C [9].

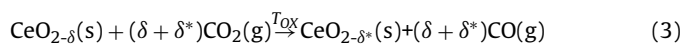
Oxygen evolution step (reduction):



Hydrogen production step (re-oxidation):



Carbon monoxide production step (re-oxidation):



\* Corresponding author.

\*\* Corresponding author at: Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, Vladimir-Prelog-Weg 1, 8093, Zurich, Switzerland.

E-mail addresses: [buechel@ptl.mavt.ethz.ch](mailto:buechel@ptl.mavt.ethz.ch) (R. Büchel), [jeroen.vanbokhoven@chem.ethz.ch](mailto:jeroen.vanbokhoven@chem.ethz.ch) (J.A. van Bokhoven).

The solar-to-fuel energy efficiency of this cycle is defined as the heating value of the product over the operation energy (solar radiative energy input and the energy to operate the system) [10]. Based on thermodynamic calculations, ceria cycle has the potential to reach up to 30% efficiency, depending on the process design [10,11]. Thus far, low amounts of hydrogen or carbon monoxide were produced experimentally, which has led to a fuel-to-solar energy efficiency of only 4%, mainly due to a partial re-oxidation to  $\text{CeO}_{2-\delta^*}$  (Eqs. (2) and (3), for  $\delta^* > 0$ ) [12]. Under certain reaction conditions, an optimization of one or both steps can lead to greater efficiency.

One approach to improve the fuel-to-solar energy efficiency of WS and CDS is to increase the number of vacancies formed during the reduction step (increase  $\delta$ ). The addition of dopants in the ceria lattice can decrease the energy of vacancy formation from 3.00 eV (pure  $\text{CeO}_2$ ) to 1.06 eV (Y-doped  $\text{CeO}_2$ ) [13]. Dopants, such as  $\text{Ti}^{4+}$ ,  $\text{Sn}^{4+}$ ,  $\text{La}^{3+}$ ,  $\text{Y}^{3+}$ ,  $\text{Sm}^{3+}$  [14],  $\text{Hf}^{4+}$  [14,15],  $\text{Zr}^{4+}$  [14,16,17], and  $\text{Cr}^{3+}$  [18], were tested in WS and CDS. Jiang et al. [14] showed that the addition of trivalent cations has a negative effect on the oxygen release, which dropped from 5.7 mL/g ( $\text{CeO}_2$ ) to 3.8 mL/g ( $\text{Ce}_{0.85}\text{Sm}_{0.15}\text{O}_2$ ), because the stable intrinsic oxygen vacancies reduce the amount of oxygen available for exchange. Cr-doped  $\text{CeO}_2$  released oxygen at 465 °C, 1000 °C lower than any other cerium-based material [14,18]; however, only a low amount of hydrogen was produced. Since chromium is the only dopant with such behaviour, we explored herein its potential at 1500 °C, to produce hydrogen and carbon monoxide.

The fuel-to-solar energy efficiency increases also if the products are formed faster at a constant energy input. Often, extended times are required (>45 min) to reach equilibrium [15]. Formation of hydrogen poisoned the surface of Sm-doped  $\text{CeO}_2$ , making CDS kinetically advantageous compared to WS [19]. The opposite was found by Chueh et al., who reported that CDS has a higher activation energy than WS, hence, the rate of CO production was lower than the rate of hydrogen production [8]. The WS rate was significantly increases in the presence of noble metals, for example, the reaction rate over Pt/ $\text{CeO}_2$  was up to 1000 times higher than over pure  $\text{CeO}_2$  [20]. Metal oxides, such as NiO and CuO, which reduce to lower valence species, also increased the hydrogen production rate from  $0.26 \cdot 10^{-8}$  ( $\text{CeO}_2$ ) to  $175 \cdot 10^{-8}$  (NiO) and  $10.7 \cdot 10^{-8}$  (CuO) mol/(s·g); the additives on the surface of ceria have a catalytic effect on the WS [20]. Metal oxides, such as chromia, on the ceria surface also promoted the oxygen storage capacity of ceria [21]. Hence, chromia shows potential for improving both the oxygen storage capacity of ceria and the hydrogen production rate and to the best of our knowledge has never been tested carbon dioxide splitting.

This study focuses on the effect of chromium addition on the activity of ceria for WS and CDS. Chromium is present in the tested materials in two forms: as a dopant introduced into the ceria lattice, or as a separate chromia phase, supported on ceria. Three methods of preparation were employed to obtain materials with phases of varying homogeneity: polymerized complex method (PCM), dry impregnation (DI), and flame spray pyrolysis (FSP). The materials were tested for WS and CDS. The addition of a chromia phase increased both hydrogen and carbon monoxide production, indicating the importance of a catalysed re-oxidation step.

## 2. Experimental

### 2.1. Preparation of the materials

The PCM-made materials were made according to an adapted method of Yashima et al. [22]. Cerium (III) acetate hydrate (Alfa Aesar, 99.9%) and chromium (III) nitrate nonahydrate (Sigma-Aldrich, 99%) were mixed and dissolved in water (100 mL); the

solution was added to a 30 mL ethylene glycol (Sigma Aldrich, >99.5%)/24 g citric acid (Acros Organics, 99.35%) solution, and the resulting mixture was heated at 180 °C until all the water had evaporated. Thereafter, the residue was heat-treated in air at 350 °C for 6 h and 800 °C for 4 h, to remove organic residues.

Dry impregnation (DI) were synthesized by dissolving chromium (III) nitrate nonahydrate (Sigma-Aldrich, 99%) in water and added to pure ceria powder, prepared by PCM. The volume of the solution was calculated so that it dry-wets the support. The mixture was dried at 100 °C, under vacuum, for 12 h and calcined at 500 °C in air for 5 h.

The FSP materials were prepared as described by Mädler et al. [23]. Cerium (III) 2-ethylhexanoate (Strem, 49% in 2-ethylhexanoic acid) and chromium (III) acetylacetonate (Fluka, 97%) were mixed and dissolved in a 2-ethylhexanoic acid (Aldrich, 99%)/toluene (Sigma-Aldrich, 99.8%) mixture (1/1 by volume) to give a 0.3 M metal concentration. The precursor solutions were sprayed at 5 mL/min and dispersed by 5 L/min oxygen (Pangas, 99%). The produced particles were collected on a glass fibre filter (Whatman GF/D, diameter 25.7 cm).

The nomenclature of the materials indicates the method of preparation (P = PCM, I = DI, and F = FSP) and the Cr content (mol%). For instance, the pure ceria prepared by PCM, is referred to as P-Ce, while FSP ceria with 10 mol% chromium is referred to as F-CeCr10. The nominal composition of the materials can be expressed as  $\text{Ce}_{1-x}\text{Cr}_x\text{O}_{2(1-x)+1.5x}$ , where  $x$  is the Cr stoichiometry so that  $0 \leq x \leq 1$ .

### 2.2. Characterization of the materials

The specific surface area ( $S_{\text{BET}}$ ) of the as-prepared materials was measured by nitrogen physisorption at 77 K in a Micromeritics TriStar unit and determined by the BET method. Before measurement, the samples were degassed at 150 °C in flowing nitrogen.

X-ray diffraction (XRD) patterns were acquired by a Bruker AXS B8 Advance diffractometer, operating with  $\text{Cu}(K_{\alpha})$  radiation. The crystal size ( $d_{\text{XRD}}$ ) was determined by the XRD patterns, based on the fundamental parameters approach incorporated in TOPAS software.

Raman spectra were measured by a Renishaw InVia Raman microscope with 514 nm at 6 mW power and an exposure time of 10 (PCM- and DI-made) and 30 s (FSP-made). The X-ray absorption near edge spectroscopy (XANES) spectra were recorded at the PHOENIX beamline from the Swiss Light Source in Villigen, Switzerland. The samples were pelletized and mounted in a vacuum chamber ( $10^{-6}$  torr) under 45° relative to the incident beam. The XANES spectra were measured at room temperature in fluorescence mode, using a four element Si solid state detector (Vortex) with 160 eV energy resolution. The X-ray beam size was  $0.5 \times 0.5$  mm and the detector dead-time was kept under 20% to exclude artifacts due to high count rates originating from the Ce L edge. The X-ray fluorescence (XRF) spectra were measured at 6.5 keV for 30 s on each pellet. The XRF spectra have been quantitatively fitted using PyMca [24], and the XANES spectra have been normalized to a post-edge value of 1 with Athena [25].

Scanning transmission electron microscopy (STEM) with elemental mapping using energy-dispersive X-ray spectroscopy (EDXS) was conducted with a FEI Talos microscope at 200 kV. An FEI ESEM XL30 was used to obtain the scanning electron microscopy (SEM) images.

### 2.3. Catalytic testing

Pellets ( $48 \pm 2$  mg and 5 mm in diameter) were made by pressing  $50 \pm 0.5$  mg of the material, at 130 bar (PCM- and DI-made) and 13 bar (FSP-made). The pellets were tested for WS or CDS in three redox cycles. An alumina reactor (99.7 Alsint, Haldenwanger

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