Master Thesis

Improving the ceria-mediated H₂O and CO₂ splitting through the addition of chromium

Author(s):
Mostrou, Sotiria

Publication Date:
2015

Permanent Link:
https://doi.org/10.3929/ethz-a-010548754

Rights / License:
In Copyright - Non-Commercial Use Permitted
Master Thesis

Improving the ceria-mediated H₂O and CO₂ splitting through the addition of chromium

Student:  Sotiria Mostrou
Examiner:  Prof. Dr. Jeroen A. van Bokhoven
Advisors:  Matthäus Rothensteiner
          Dr. Robert Büchel
          Prof. Dr. Sotiris E. Pratsinis

September 2015
# Table of Contents

Abstract ................................................................................................................................ V

1. Introduction ................................................................................................................. 7
   1.1. H₂O and CO₂ Splitting. ..................................................................................... 7
   1.2. Doping of CeO₂ ............................................................................................... 8
   1.3. Addition of Co-catalyst on CeO₂ ................................................................. 9
   1.4. Objective ......................................................................................................... 9

2. Experimental ............................................................................................................. 10
   2.1. Preparation of the Catalysts ........................................................................... 10
   2.2. Characterization of the Catalysts ................................................................. 10
   2.3. Catalytic Testing ............................................................................................. 11

3. Results and Discussion .............................................................................................. 12
   3.1. Characterization of the Catalysts ................................................................. 12
   3.2. O₂ Evolution .................................................................................................. 17
   3.3. H₂ Production ................................................................................................ 18
   3.4. CO Production .............................................................................................. 19
   3.5. Proposed Reaction Mechanism ..................................................................... 20

4. Conclusions ............................................................................................................... 23

5. Outlook .................................................................................................................... 23

6. Acknowledgements ................................................................................................. 24

7. Declaration of Authorship ....................................................................................... 24

8. References ............................................................................................................... 25

Appendix .................................................................................................................... 26
Abstract

The solar thermochemical H$_2$O and CO$_2$ splitting, mediated by ceria, shows a great potential for the production of “green” syngas. However, only a small amount was produced experimentally, hampering any industrialization. Herein, chromium was added in the CeO$_2$-system to improve the production of syngas. The catalysts were characterized by X-ray diffraction, Raman spectroscopy, and electron microscopy. They were tested for H$_2$O and CO$_2$ splitting, respectively. The catalysts synthesized by polymerized complex method and dry impregnation consisted of two crystal phases, CeO$_2$ and Cr$_2$O$_3$. The catalysts made by flame spray pyrolysis exhibited a homogeneous Cr-doped CeO$_2$ phase, while the Cr$_2$O$_3$ phase was found only above 25 mol% Cr content. The catalysts with the Cr$_2$O$_3$ phase improved greatly both the H$_2$ and CO production rate, which increased by a factor of 20 and 500, respectively. During the redox cycling, the Cr$_2$O$_3$ was probably reduced to metallic chromium. The proposed mechanism introduces a new approach, where the catalytically active sites are formed in situ. Following this approach, further metal oxides could be considered as potential co-catalysts for the H$_2$O and CO$_2$ splitting.
1. Introduction

1.1. H₂O and CO₂ Splitting

Liquid fuels, produced in an environmentally friendly way, are very important in the attempt to meet the increasing energy demand while restraining the emissions of anthropogenic CO₂.[1] Solar thermochemical water splitting (WS) and carbon dioxide splitting (CDS) require solar radiation[2] to produce hydrogen and carbon monoxide from carbon dioxide and water.[3] The H₂ can be used as fuel without further treatment, or it can be used together with CO (syngas) to produce liquid solar fuels and other chemicals by Fischer-Tropsch synthesis.[4] The WS and CDS reactions can be realized by means of a reduction-oxidation (redox) cycle of materials with a high oxygen exchange capacity, like CeO₂. The latter is used for high temperature (above 1,400 °C) separate[5] or simultaneous[6] WS and CDS. The WS and CDS mechanisms are similar, in that they include a redox cycle as shown in equations 1 to 3. Thus far, the low H₂ and CO production has led to a fuel-to-solar energy efficiency of only up to 4%, mainly due to only a partial re-oxidation to CeO₂−δ (equations 2a and b).[7] A theoretical full re-oxidation to CeO₂ (equations 3a and b) would maximize the efficiency. Under certain reaction conditions, an optimization of one or both steps can lead to greater efficiency.

O₂-evolution step (reduction of ceria):

\[
\text{CeO}_2 (s) \xrightarrow{T_{\text{red}}} \text{CeO}_{2-\delta} (s) + \frac{\delta}{2} \text{O}_2 (g)
\] (1)

H₂-production step (re-oxidation of ceria):

\[
\begin{align*}
\text{CeO}_{2-\delta} (s) + (\delta - \delta^*) \text{H}_2 \text{O}(g) & \xrightarrow{T_{\text{ox}}} \text{CeO}_{2-\delta'} (s) + (\delta - \delta^*) \text{H}_2 (g) \\
\text{CeO}_{2-\delta} (s) + \delta \text{H}_2 \text{O}(g) & \xrightarrow{T_{\text{ox}}} \text{CeO}_2 (s) + \delta \text{H}_2 (g)
\end{align*}
\] (2a, 3a)

CO-production step (re-oxidation of ceria):

\[
\begin{align*}
\text{CeO}_{2-\delta} (s) + (\delta - \delta^*) \text{CO}_2 (g) & \xrightarrow{T_{\text{ox}}} \text{CeO}_{2-\delta'} (s) + (\delta - \delta^*) \text{CO}(g) \\
\text{CeO}_{2-\delta} (s) + \delta \text{CO}_2 (g) & \xrightarrow{T_{\text{ox}}} \text{CeO}_2 (s) + \delta \text{CO}(g)
\end{align*}
\] (2b, 3b)
**Introduction**

**Figure 1.** The redox cycle of ceria-mediated solar thermochemical H$_2$O and CO$_2$ splitting. Fresh CeO$_2$ (grey pathway) is heated up to 1,500 °C, in the presence of argon, and reduces into the non-stoichiometric CeO$_{2-\delta}$ (red pathway). The reduced intermediate is cooled down to 800 °C where a flow of H$_2$O and/or CO$_2$, diluted in Ar, is introduced, which results in the re-oxidation of CeO$_{2-\delta}$, while H$_2$ and/or CO is produced (blue and green pathway). The non-stoichiometry $\delta$ increases during reduction and decreases during re-oxidation. Experimentally, only partial re-oxidation to CeO$_{2-\delta^*}$ is observed (blue pathway). The optimal re-oxidation step is represented by the green pathway and leads to full re-oxidation to CeO$_2$ ($\delta^* = 0$).

1.2. **Doping of CeO$_2$**

One approach to improving the fuel-to-solar energy efficiency of WS and CDS is to increase the number of vacancies that form during the reduction step (increase $\delta$). The addition of dopants inside the CeO$_2$ can decrease the energy of vacancy formation from 3.00 eV (un-doped CeO$_2$) to 1.06 eV (Y-doped CeO$_2$).\cite{8} Dopants such as Ti$^{4+}$, Sn$^{4+}$, La$^{3+}$, Y$^{3+}$, Sm$^{3+}$,\cite{9} Hf$^{4+}$,\cite{9-10} Zr$^{4+}$,\cite{9, 11} and Cr$^{3+}$\cite{12} were tested in WS and CDS. Jiang *et al.* showed that the addition of trivalent cations had a negative effect on the release of O$_2$, which, at 1,500 °C, decreased from 5.7 mL/g (CeO$_2$) to 3.8 mL/g (Ce$_{0.85}$Sm$_{0.15}$O$_2$) because stable intrinsic oxygen vacancies were formed, which reduced the amount of the oxygen that is available for exchange. In contrast, Cr-doped CeO$_2$ released oxygen at 1,000 °C lower than any other cerium-based catalysts;\cite{9, 12} however, a negligible amount of H$_2$ was produced. Since Cr is the only dopant that behaves in this way, we explored its potential at higher reaction temperatures (1,500°C) for the production of both H$_2$ and CO.
1.3. **Addition of Co-catalyst on CeO$_2$**

Another approach to improving the fuel-to-solar energy efficiency is to enhance the re-oxidation step, which depends primarily on the reaction kinetics of WS and CDS. The formation of H$_2$ poisoned the surface of Sm-doped CeO$_2$, making CDS kinetically advantageous compared to WS.$^{[13]}$ The opposite was found by Chueh et al., who reported that CO$_2$ dissociation has a higher activation energy than H$_2$O, hence, the rates of H$_2$ production were higher.$^{[6]}$ In general, a fast reaction rate of the re-oxidation step is desirable so that product formation does not inhibit further re-oxidation. There was a significant increase in the rate of WS in the presence of noble metals, for example the reaction rate over Pt/CeO$_2$ was up to 1,000 times higher than over pure CeO$_2$.\(^{[14]}\) Otsuka et al. showed that metal oxides, such as NiO and CuO, which reduce to lower valence species, also increase the H$_2$ production rate from 0.26$\cdot 10^{-8}$ (CeO$_2$) to 175$\cdot 10^{-8}$ (NiO) and 10.7$\cdot 10^{-8}$ (CuO) mol/(s$\cdot$g); the additives on the surface of CeO$_2$ have a catalytic effect on the WS.$^{[14]}$ Other metal oxides, with the potential to reduce during reaction conditions, could catalyse the H$_2$O and CO$_2$ splitting accordingly. Cr$_2$O$_3$ seems very promising, as it reduces above 700 °C,$^{[15]}$ and to the best of our knowledge has never been tested for H$_2$O and CO$_2$ splitting.

1.4. **Objective**

This thesis focused on the effect of the addition of chromium on the catalytic activity of CeO$_2$ with regard to WS and CDS. Chromium is added in two forms: as a dopant introduced into the CeO$_2$ lattice, or as a separate Cr$_2$O$_3$ phase supported on CeO$_2$. Three methods of preparation were chosen with the aim of obtaining 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 chromia had a significant effect on both H$_2$ and CO production. The increased production rates indicate the importance of a catalysed re-oxidation step.
2. Experimental

2.1. Preparation of the Catalysts

Cr-containing CeO₂ catalysts were prepared by three methods. 1) The PCM catalysts, according to an adapted method of Yashima et al.\textsuperscript{[16]} cerium (III) acetate hydrate (Alfa Aesar, 99.9%) and chromium (III) nitrate nonahydrate (Sigma-Aldrich, 99%) were mixed and dissolved in H₂O (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 at 350 °C in air for 6 h followed by calcination at 800 °C in air for 4 h. 2) DI was used to produce Cr₂O₃ supported on CeO₂: chromium (III) nitrate nonahydrate (Sigma-Aldrich, 99%) was dissolved in H₂O and added to pure CeO₂ powder, prepared by PCM. The mixture was heated at 100 °C, under vacuum, for 12 h and calcined at 500 °C in air for 5 h. 3) The FSP catalysts were prepared as described by Mädler et al.\textsuperscript{[17]} cerium (III) 2-ethylhexanoate (Strem, 49% in 2-ethylehexanoic 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 (5 mL/min) 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 catalysts indicates the method of preparation (P = PCM, I = DI, and F = FSP) and the Cr content (mol%). For instance, the pure CeO₂ prepared by PCM, is referred to as P-Ce, while FSP CeO₂ with 10 mol% Cr is referred to as F-CeCr10. The actual composition of the materials can be expressed as Ce₁₋ₓCrₓO₂(₁₋ₓ)+1.₅ₓ, where x is the Cr stoichiometry so that 0 ≤ x ≤ 1.

2.2. Characterization of the Catalysts

The specific surface area (\(S_{\text{BET}}\)) of the as-prepared catalysts was measured by N₂ physisorption at 77 K in a Micromeritics TriStar unit and determined by means of the BET method. Before the measurement, the samples were degassed at 150 °C in a flow of N₂. X-ray diffraction (XRD) patterns were acquired by a Bruker AXS B8 Advance diffractometer, operating with Cu(Kα) radiation. The resulting peaks were analysed by 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) and 30 s (FSP). Scanning transmission
electron microscopy (STEM) analysis with elemental mapping using energy-dispersive X-ray spectroscopy (EDXS) was conducted with a FEI Talos microscope operated at 200 kV.

2.3. Catalytic Testing

Pellets (48±2 mg and 5 mm in diameter) were made by pressing 50±0.5 mg of catalyst, at 130 bar (PCM and DI) and 13 bar (FSP). The pellets were tested for WS or CDS in three redox cycles. An alumina reactor (99.7 Alsint, Haldenwanger Ceramics, 9.5×12.7×400 mm) was heated in an electric infrared furnace (Ulvak VHT E44). The reduction step at 1,500 °C lasted 10 min; the total flow was 100 mL/min Ar (Air Liquide, 99.999%). The oxidation step at 800 °C lasted 10 min; the total flow was 100 mL/min Ar + 0.4 g/h H₂O vapour (injected at 120 °C) for WS, and 100 mL/min Ar + 8.4 mL/min CO₂ (Air Liquide, 99.999%) for CDS. The redox cycles were performed under ambient pressure; the heating and cooling rates were 50 and 100 °C/min, respectively. The product stream passed through a water trap immersed in an ice bath to condense H₂O and was analysed online with an OmniStar mass spectrometer (MS) from Pfeiffer Vacuum. After each test, the O₂ and H₂ MS signals were calibrated with two standards (250.0 ppm O₂ in Ar and 0.50% H₂ in Ar (Air Liquide)) to quantify the amounts of O₂ and H₂ produced during testing. The produced CO was quantified by a Bruker Vector 22 FT-IR Spectrometer, recording from 4,000 to 400 cm⁻¹, connected in parallel to the MS.
3. Results and Discussion

3.1. Characterization of the Catalysts

Figure 2 presents the crystal size (a) and the specific surface area (b) of the catalysts, determined by XRD and N\textsubscript{2} physisorption, respectively. The as-prepared FSP catalysts had a much smaller (10 nm) crystal size than the PCM and DI catalysts (40 nm). After the catalytic tests, the crystal size had increased by a factor of 2 (PCM) and 7 (FSP). The FSP catalysts sintered from 10 to 50 nm in the absence of chromium, while its presence promoted sintering up to 75 nm. All the wet-produced catalysts sintered from 40 to 80 nm, independent of Cr content. The crystal size of the FSP catalysts was smaller than the crystal size of the wet-produced catalysts, both before and after the catalytic test. The wet-produced catalysts (P-CeCr X and I-CeCr X) had a ten times lower $S_{\text{BET}}$ (<15 m\textsuperscript{2}/g) than the flame-produced catalysts (F-CeCr X). The $S_{\text{BET}}$ of the FSP powders ranged from 116 to 147 m\textsuperscript{2}/g. The samples containing chromium had a lower surface area, independent of the preparation method. Flame-produced Zr-doped CeO\textsubscript{2} showed a comparable surface area and a similar trend after the addition of dopant\cite{18} in contrast to reports of an increase in the surface area with the addition of dopants\cite{19,19}.

Figure 3a depicts the XRD patterns of pure and 15 mol\% Cr-containing CeO\textsubscript{2} catalysts. The XRD patterns of all the tested catalysts are shown in Appendix A 1. All XRD patterns have the characteristic CeO\textsubscript{2} fluorite structure. There was a Cr\textsubscript{2}O\textsubscript{3} phase in the Cr-containing wet-prepared samples (P-CeCr15 and I-CeCr15), as seen in the magnification of the 33 to 40° 2\theta region, while Cr\textsubscript{2}O\textsubscript{3} was not detected in the F-CeCr15 catalyst. Moriceau et al. indicated that Cr\textsubscript{2}O\textsubscript{3} phase dominates in Cr/CeO\textsubscript{2} materials with high surface coverage of Cr species.\cite{20}

Figure 3b illustrates the XRD patterns of the catalysts after three redox cycles. All Cr-containing catalysts show the characteristic peaks of the perovskite-like CeCrO\textsubscript{3} structure. A similar observation was reported for spent Cr-doped CeO\textsubscript{2}.\cite{21} Cr\textsubscript{2}O\textsubscript{3} was unstable during the redox cycles, as found for the spent P-CeCr15 and I-CeCr15. This may be due to the partial or complete incorporation of chromium in the lattice or due to reduction of Cr\textsuperscript{3+} to Cr species with lower valence, undetectable by XRD. Additional peaks of aluminium species, such as AlCe and Al\textsubscript{2}O\textsubscript{3}, are present, due to the interaction with the alumina sample holder. The peak at 26° 2\theta, characteristic of non-stoichiometric CeO\textsubscript{2-\delta} and observed on F-Ce, indicates the incomplete re-oxidation of CeO\textsubscript{2}, even after exposure to air at room temperature.
Figure 2. a) Crystal size ($d_{XRD}$) and b) specific surface area ($S_{BET}$) as a function of Cr content of the as-prepared (solid line) and spent (dash line) PCM (■), DI (▲), and FSP (●) catalysts.

The state of the chromium in the as-prepared catalysts was investigated with Raman spectroscopy (Figure 4a): The main peak of CeO$_2$ at 460 cm$^{-1}$ is visible in all spectra. The additional peak at 552 cm$^{-1}$ in the P-CeCr15 and I-CeCr15 spectra was assigned to Cr$_2$O$_3$, as shown in the Raman spectra of pure Cr$_2$O$_3$ (commercial powder from Strem Chem.). The FSP catalysts show a peak at 842 cm$^{-1}$, identified as the CrO$_{4}^{2-}$ in the CeO$_2$ lattice, indicating that the flame-produced CeO$_2$ catalysts were doped with Cr$^{[12]}$; only at high Cr content was Cr$_2$O$_3$ detected in flame-produced catalysts (F-CeCr25). The interpretation of the Raman spectra and the XRD patterns of the as-prepared catalyst confirm that chromium in the PCM and DI catalysts was only present as bulk Cr$_2$O$_3$, while FSP resulted in mainly doped materials. The PCM preparation was unsuitable for doping CeO$_2$ with chromium. It required calcination in air at 800 °C to remove the residual organic compounds; when Cr-doped CeO$_2$ (F-CeCr15) was calcined at 800 °C, the characteristic Cr$_2$O$_3$ peak was found in the Raman spectra, replacing the lattice CrO$_{4}^{2-}$ (Appendix A 2). The calcination step caused leaching of the doped Cr to the surface and the formation of a Cr$_2$O$_3$ phase.
Results and Discussion

Figure 3. XRD patterns of the PCM (P-Ce, P-CeCr15), DI (I-CeCr15), and FSP (F-Ce, F-CeCr15) a) as-prepared and b) spent catalysts. The peaks correspond to CeO\(_2\) (♦, ICSD 28709), Cr\(_2\)O\(_3\) (▼, ICSD 75577), CeCrO\(_3\) (●), CeO\(_2\)-δ, and Ce/Al species (AlCe, Al\(_2\)O\(_3\)). XRD patterns of P-CeCr15, I-CeCr15, and F-CeCr15 are magnified from 33 to 40° 2θ.
Results and Discussion

Figure 4. Raman spectra of a) as-prepared and b) spent catalysts. Commercial Cr$_2$O$_3$ is presented as reference. The peak at 553 cm$^{-1}$ (▼) corresponds to the Cr$_2$O$_3$ phase and the peak at 842 cm$^{-1}$ (●) to chromate ion inside the CeO$_2$ lattice.

Figure 4b shows the Raman spectra of the spent catalysts. The peaks of Cr$_2$O$_3$ and CrO$_{4}^{2-}$ were absent, and only CeO$_2$ was observed, with the exception of F-CeCr15, which exhibited many peaks; the peaks between 200 and 438 cm$^{-1}$ are similar to those of the perovskite structure LCrO$_3$ (L=lanthanides).[22] The absence of Cr$_2$O$_3$ in the spent I-CeCr15 and P-CeCr15 catalysts clearly indicated its instability under the reaction conditions, as also revealed by XRD (Figure 2b). However it is unlikely that all the chromium entered the CeO$_2$ lattice as no other peaks were observed.

STEM combined with EDXS were used to visualize the Cr and Ce in the as-prepared catalysts (Figure 5a) and of the spent I-CeCr15 (Figure 5b). An inhomogeneous distribution of Cr (green) and Ce (red) was observed in the P-CeCr15 and I-CeCr15 catalysts. Due to the partial overlap of the Cr signal and the second Ce line, Cr seems to be present all over the map but is actually present only at the bright green sites. The size of the chromium-rich areas varies from 200 to 500 nm (P-CeCr15) and from 5 to 100 nm (I-CeCr15). F-CeCr15 and F-CeCr25 exhibited a homogeneous distribution of elements, with small (5-10 nm) chromium areas present only in F-CeCr25. This finding supports the XRD and Raman measurements (Figures 3a and 4a), where supported Cr$_2$O$_3$ was found only in the P-CeCr15, I-CeCr15 and F-CeCr15 catalysts. The spent I-CeCr15 retained some Cr species; the maps of the spent catalysts were similar (Appendix A 3). The distinct chromium sites in the element mapping of
the spent catalysts supports the hypothesis that reduced Cr species are formed under the reaction conditions but are not traceable by XRD or Raman spectroscopy.

Figure 5. Distribution of Ce (red) and Cr (green) elements of a) the as-prepared P-CeCr15, I-CeCe15, F-CeCr15, and F-CeCr25, and b) the spent I-CeCr15. In each row the first image is of both Ce and Cr, the second of only the Ce species and the third of only the Cr species. The images were obtained by STEM coupled with EDXS mapping.
3.2. O₂ Evolution

Figure 6a shows the O₂ mass spectroscopy signal during the first heating-up to 1500 °C, over pure CeO₂ and 15 mol% Cr containing CeO₂ catalysts. All catalysts had the maximum O₂ evolution at around 1500 °C. Only Cr-doped CeO₂ (F-CeCr15) exhibited a second O₂ evolution peak already at 423 °C. This low temperature O₂ evolution has been observed by Singh et al.\cite{12, 21} They identified that lattice O₂ starts releasing at 300 °C resulting from the reduction of both Ce⁴⁺ and Cr³⁺ species, which lead to the formation of a mixture of perovskite like CeCrO₃ and fluorite like CeO₂₋ₓ. The Cr₂O₃ supported on CeO₂ catalysts (P-CeCr15 and I-CeCr15) exhibited similar O₂ release behaviour as pure CeO₂ catalysts, where there is no O₂ evolution at 300 °C, possible due to the absence of Cr-Ce lattice interactions. Figure 6b illustrates the O₂ evolution rate, normalized by the amount of CeO₂ present in each catalyst. The presence of Cr increased the amount of O₂ released. An exponential increase was observed for Cr-doped CeO₂ catalysts (F-CeCr X), which can be attributed to the second O₂ evolution peak at 450 °C and the formation of CeCrO₃ observed by XRD. Cr₂O₃/CeO₂ catalysts (P-CeCr X, and I-CeCr X) exhibited a linear O₂ increase which could not be associated with Cr-Ce interactions in the lattice as in the case of Cr-doped CeO₂, hence it should originate from the reduction of Cr in the bulk Cr₂O₃ phase. Cr³⁺ can reduced to Cr²⁺ (equation 4) forming CrO, which above 550 °C decomposes to metallic Cr and Cr₂O₃ (equation 5).\cite{23} Assuming that all the excess O₂ released was due to the reduction of Cr³⁺ to Cr²⁺, then the amount of metallic Cr that could be present on the spent catalysts was 1.6 wt%. Metallic Cr oxidizes in the presence of O₂ even at room temperature.\cite{23} The trace amount of Cr⁰ and its rapid oxidation could explain its absence on both XRD patterns and Raman spectra of the spent catalysts (Figures 3b and 4b).

\[
\begin{align*}
\text{Cr}_2\text{O}_3 (s) \overset{1500 \, ^\circ\text{C, low p}_2\text{O}_2}{\longrightarrow} 2\text{CrO}(s) + \frac{1}{2}\text{O}_2 (g) \\
3\text{CrO}(s) \overset{\geq 500 \, ^\circ\text{C, vacuum}}{\longrightarrow} \text{Cr}(s) + \text{Cr}_2\text{O}_3 (s)
\end{align*}
\]
Results and Discussion

Figure 6. a) Oxygen formation during heating up of pure CeO$_2$ (dotted lines) and 15 mol% Cr/CeO$_2$ (solid lines). Oxygen maximums are observed at 423 and 1450 °C. b) O$_2$ evolution rate during the first cycles as function of Cr content. The volume of O$_2$ release has been normalized by the mass of CeO$_2$ present in the Cr/CeO$_2$ catalyst.

3.3. H$_2$ Production

Hydrogen is produced as a result of the re-oxidation of CeO$_2$-$\delta$ (equation 2a). Figure 7a represents the H$_2$ mass spectroscopy signal during the oxidation step of the PCM and FSP materials. In the absence of Cr$_2$O$_3$ (P-Ce, F-Ce, and F-CeCr10 and 15), the H$_2$ signals reached a maximum at 1.3$\cdot$10$^{-10}$ mA, which decreased very slowly and did not return to the baseline (8$\cdot$10$^{-11}$ mA) after 10 min in a stream of H$_2$O; the CeO$_2$-$\delta$ was not fully re-oxidized and had the potential to produce H$_2$ for more than 10 min. The slow WS kinetics over pure CeO$_2$ limit H$_2$ production in technical applications. On the other hand, the samples that contain a distinctive Cr$_2$O$_3$ phase (P-CeCr10, 15, 30, I-CeCr15 and F-CeCr25) exhibited an accelerated WS step with a very high maximum peak at 4.6$\cdot$10$^{-9}$ mA, which decreased sharply and returned to the baseline in less than 3 min. After that time no H$_2$ was produced due to the lack of oxygen vacancies.
Results and Discussion

Figure 7. a) Time-resolved H₂ production during the oxidation step ($t_{ox} = 10$ min) of PCM (top) and FSP (bottom) catalysts with different amounts of Cr. b) Rates of H₂ production of PCM (■), DI (▲), and FSP (●) as a function of chromium content.

Figure 7b presents the H₂ production rate, obtained by the quantification of the H₂ produced in one step, normalized by the mass of the catalyst and the time, during which H₂ is produced, for examples P-Ce produced H₂ during 10 min, while I-CeCr15 produced it for 2 min. The total H₂ produced in one cycles is presented in Appendix A 4 and it seemed to be stable for 5 cycles. The preparation method had an effect of the activity of pure CeO₂: F-Ce produced 1.8 times more H₂ than P-Ce. The effect of Cr₂O₃ was clear. The rate of H₂ production increased from 0.09 mL/(g·min) (P-Ce) to 1.94 mL/(g·min) (I-CeCr15), exhibiting an improvement of 21 times. This effect was also observed over F-CeCr25, the only FSP catalyst containing Cr₂O₃, which produces 1.65 mL/(g·min) H₂, and over all the Cr-containing PCM catalysts, which produce 1.19 to 1.41 mL/(g·min) H₂. Based on EDXS, the size of the Cr aggregates had an effect on the production of H₂; the most superior catalysts were those with smaller chromium aggregates, I-CeCr15 and F-CeCr25 (Figure 5). Cr₂O₃ caused a significant increase (×21) in the rate of H₂ production but not on the corresponding rate of O₂ evolution (×3), indicating that only the re-oxidation step was significantly influenced.

3.4. CO Production

Pure and 15 mol% Cr-containing CeO₂ were tested for CDS. Figure 8a presents the CO production during one oxidation step. The rate of CO production exhibited similar patterns as the rate of H₂ production (Figure 7a). Pure and Cr-doped CeO₂ reached an insignificant
maximum production ($<1 \cdot 10^{-3}$ vol%), which decreased slowly but had still not reached the baseline even after 10 min in a stream of CO₂. However, over Cr₂O₃/CeO₂ catalyst (I-CeCr15), the peak CO production was significant ($8.4 \cdot 10^{-3}$ vol%) and full production was reached within 3.5 min.

**Figure 8.** a) Time-resolved CO production during the oxidation step ($t_{ox} = 10$ min) of DI (top) and FSP (bottom) with pure and 15 mol% Cr/CeO₂. b) Rates of CO production of DI (▲) and FSP (●) as a function of chromium content.

Figure 8b gives the rates CO production. Negligible amounts of CO formed over P-Ce (0.005 mL/(g·min)), in contrast to nanosized F-Ce which resulted in 41 times more CO (0.21 mL/(g·min)). Improved CO production (up to 0.66 mL/(g·min)) was observed also over Cr-doped CeO₂ (F-CeCr15) (0.66 mL/(g·min)). The most significant effect was observed over the I-CeCr15 catalyst: the rate of CO production increased by 3 orders of magnitude (2.50 mL/(g·min)) compared to P-Ce and was twice as high as the best reticulated porous ceramic CeO₂.[24]

### 3.5. Proposed Reaction Mechanism

Figure 9a compares the rates of H₂ and CO production. The best performing CeO₂-based system is the onecontending Cr₂O₃, which probably reduces to metallic chromium during the reduction step. The rate of H₂ and CO production exhibited a 20 and 500 times improvement, respectively, compared to the commonly used CeO₂. This indicates the significance of a
Results and Discussion
catalysed re-oxidation step. The presence of the co-catalyst influences the reaction mechanism in the proposed way illustrated in Figure 9b.

Figure 9. a) Comparison of the rates of H₂ and CO production over pure, Cr-doped and Cr₂O₃ supported CeO₂. b) The proposed reaction mechanism of the best performing catalyst (Cr₂O₃/CeO₂). Cr₂O₃/CeO₂ reduces during the reduction step to Cr⁰/Cr₂O₃/CeO₂₋ₓ. During the re-oxidation, Cr⁰ reduces the H₂ desorption energy (WS) and the CO₂ dissociation energy (CDS).

In WS, the H₂ formed poisons the surface, inhibiting further re-oxidation. Hansen et al. demonstrated the mechanism of the re-oxidation of reduced ceria during WS. By density function theory (DFT) calculations, they showed that the most energy-demanding step of WS is evolution of H₂ from the surface, with an energy barrier of 3eV. Hence, H₂ is more likely to desorb from low coordinated defect sites or from spill-over to noble metal pits. The spill-over effect was observed for additives such as the noble metals Pd and Pt and the metal oxides NiO and CuO, which reduced during the reaction. The desorption of H₂ from low coordinated defect sites may explain the improved H₂ production observed for CeO₂ with a 10 nm particle size (F-Ce). The spill-over effect could explain the significant performance in the presence of small Cr₂O₃ aggregates: Cr₂O₃ reduces to Cr metal under the strong reduction conditions; hydrogen atoms spill-over from CeO₂ to Cr, from where it desorbs as H₂. The mechanism of H₂ desorption by hydrogen spill-over was demonstrated in the presence of metals
Results and Discussion

(Pt/CeO₂) based on DFT calculations;[27] it is similar to the dehydrogenation and water gas shift reaction mechanism.

In CDS, Chueh et al. found that over pure CeO₂, CO₂ dissociation has a higher activation energy (0.8 eV) than H₂O dissociation (0.5 eV),[6] but the presence of a dopant switched the kinetics, making CDS faster than WS.[13] Hence, metallic Cr atoms on the surface, formed as described in WS, may aid in the dissociation of CO₂ to CO and O atoms, after which the oxygen atom spill-over from Cr to fill the nearest oxygen vacancy in ceria.

Changes in the surface area will also affect the production of hydrogen and carbon monoxide. Chromium influenced the sintering of the primary particles. The mean size of the primary particles of the spent catalysts was detected by scanning electron microscopy. Chromium significantly influenced the mean particle size, which reduced from 53.8 μm (P-Ce) to 1.5 (I-CeCr15) and 2.1 (P-CeCr15 and F-CeCr15). However, there was no correlation with the enhanced rates of hydrogen and carbon monoxide production (Appendix A 5).

The addition of the co-catalyst clearly influences significantly the production of both H₂ and CO, and it is an effortless way to improve the performance of any ceria-based system used for WS and CDS. Until now, mostly noble metals were considered towards WS, as they are known to desorb H₂. However, they are economically inefficient for a commercialized solar thermochemical H₂O and CO₂ splitting process. Metal oxides, although cheaper and easily accessible, have not been considered as co-catalysts, since the O-H bond forming on their surface prohibits H₂ desorption, i.e., slow reaction kinetics over CeO₂. However, CuO, NiO and Cr₂O₃ have been found highly active for WS, because they probably reduce to their metallic form during the reduction step.[14] To the best of our knowledge, this is the first time that an oxide co-catalyst has been tested in CDS. Although CDS mechanism is not as exploited as WS, it seems to be also positively influenced by the presence of Cr₂O₃. The proposed mechanism, which explains the observations of this study and of Otsuka et al., introduces a new approach towards the improvement of WS and CDS that is enhanced by the in situ formation of the co-catalyst.
4. Conclusions

Chromium containing CeO$_2$ catalysts were prepared by three different production methods and tested for the synthesis of “solar” H$_2$ and CO. Cr-doped CeO$_2$ catalysts were produced by flame spray pyrolysis with high surface area, up to 100 m$^2$/g. Cr$_2$O$_3$ supported on CeO$_2$ were produced with the polymerized complex method and dry impregnation, resulting in Cr$_2$O$_3$/CeO$_2$ mixture, with chromia cluster size of 5 to 500 nm. The nanoparticles of CeO$_2$, synthesized by FSP, produced almost twice the amount of H$_2$ compared to PCM CeO$_2$, while the CO production rate was increased up to 42 times. H$_2$ and CO production rates were increased over all Cr containing catalysts but significantly higher production rates were observed for catalysts containing a distinct Cr$_2$O$_3$ phase: 1.94 and 2.5 mL/(g$\cdot$min), respectively. During the reaction conditions, Cr$_2$O$_3$ was likely reduced to metallic Cr, which could catalyse the splitting reaction by reducing the high energy barriers of H$_2$ desorption and CO$_2$ dissociation. The significantly improved production rates are similar to those observed in the presence of expensive noble metals, such as Pt, reducible metal oxides as attractive candidate as co-catalyst for the ceria-mediated H$_2$O and CO$_2$ splitting.

5. Outlook

In this study, the catalyst were tested for WS and CDS cycles separately. The effect of the catalysts should be also studied in a simultaneous WS and CDS, to evaluate the possibility of an enhanced direct production of H$_2$ and CO (syngas). The evaluation of the stability of Cr$_2$O$_3$/CeO$_2$ system in a long term cycling ($\geq$ 200 cycles) is essential before any attempt for scaling-up. Furthermore, the study should be expand to other transition metal oxides, which have the potential to reduce to their metallic form during the reduction step. Specifically, manganese and iron oxides seem to be very promising candidates to replace Cr$_2$O$_3$, as they have the potential to reduce during the reaction. On the other hand, non-reducible oxides should also be studied in order to provide a dipper comprehension of the catalytic mechanism and a stronger proof of the superiority of the reducible metal oxides. Dr. Büchel has been dedicated into the study of more oxide-based systems in order to provide an alternative for Cr$_2$O$_3$ and a possibly a more active catalyst and Mr. Rothensteiner approaches the topic of structural properties with in situ and operando characterization techniques.
6. Acknowledgements

Firstly, my earnest gratitude goes to Professor van Bokhoven for giving me the opportunity for work on this project. His encouraging words and structured comments were always welcome inputs. Secondly, my sincerest appreciation goes to Professor Pratsinis for believing in the potential of this project and agree in this fruitful collaboration. My heartiest gratitude goes to Dr. Büchel and Mr. Rothensteiner, who were always available for enquiries and provided extensive support. Without their suggestions and their deep knowledge on nanomaterials and thermochemical splitting, it would not have been possible to materialize this work. Furthermore, my earnest appreciation goes to Dr. Krumeich for the valuable microscopy images and the electron microscopy centre for providing the necessary infrastructure. I also take this opportunity to express a deep sense of gratitude to Hellenic Petroleum, for the scholarship given to me to fulfil my Master studies, during which this Thesis was conducted. Finally, I would like to thank my loved ones for their endless love, support, and comprehension.

The research leading to these results has received funding from the Swiss Competence Centre Energy & Mobility and from the European Research Council under the European Union's Seventh Framework Program (FP7/2007-2013) / ERC grant agreement n° 247283.

7. Declaration of Authorship

I hereby certify that this project has been composed by me and is based on my own work, unless stated otherwise. No other person’s work has been used without due acknowledgement in this Thesis. All references and verbatim extracts have been quoted, and all sources of information, including graphs and data sets, have been specifically acknowledged.

Sotiria Mostrou
8. References

Appendix

A1. XRD patterns of the as-prepared catalysts tested for WS and CDS.
A 2. Raman spectra of Cr-doped CeO₂ (F-CeCr15) before and after calcination at 800 °C.
A 3. Distribution of Ce (red) and Cr (green) elements of the spent P-CeCr15, I-CeCe15, and F-CeCr15. In each row the first image is of both Ce and Cr, the second of only the Ce species and the third of only the Cr species. The images were obtained by STEM couples with EDXS mapping.
A 4. H₂ total production in each of 5 cycles, over P-CeO₂, F-CeCr15, and I-CeCr15.
A 5. H2 and CO production rate as a function of the primarily particle size of the spent catalysts. The primarily particle size was obtained from SEM pictures of the catalysts after 3 redox cycles. The points correspond to P-Ce (■), P-CeCr15 (□), I-CeCr15 (▲), and F-CeCr15 (●).