

Supporting information for the article

Solvent-Free Synthesis of Rechargeable Solid Oxygen Reservoirs for Clean Hydrogen Oxidation

G. Rothenberg*, E. A. de Graaf, A. Blik

*Chemical Engineering Department, University of Amsterdam,
Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands.
Fax. +31 20 525 5604.
E-mail: gadi@science.uva.nl*

Experimental Section

GC analysis was performed at 50 °C on a Carlo Erba 4300 gas chromatograph modified with a with a 16-way valve to enable fast sampling and a 3 m Alltech Unibead 1S column, using 1 mLmin⁻¹ N₂ (99.5%, Hoekloos) as internal standard. Selective MS analysis was performed using a Pfeiffer QMA 200 mass spectrometer (m/z range 0–100). Powder XR diffraction measurements were performed using a Philips x-ray diffractometer with a vertical goniometer. A Cu tube was used as the radiation source ($\lambda = 1.54 \text{ \AA}$). The x-ray beam was passed through a Ni filter (no monochromator was used) and the scattered beam was recorded with a proportional Xe filled detector, with a 2 θ step size of 0.005°. Surface parameters were measured on a Thermo Finnigan Sorptomatic 1990 instrument using N₂ adsorption. Unless noted otherwise, all chemicals were purchased from commercial firms and used as received. Ethylene (99.7% pure), He (99.996%), O₂ (99.5%, dried over molecular sieves before use), and H₂ (99.999%, purified by a BTS column and dried over molecular sieves before use) were purchased from Praxair. Ethane (99.3%) was purchased from Ucar. All gas streams were dried using a Perma Pure MD-050-72S membrane prior to GC analysis. The mixed oxides **1–10** were prepared from the corresponding metal nitrate hydrate precursors, except for Ce_{0.9}V_{0.1}O_y, Ce_{0.9}W_{0.1}O_y and Ce_{0.9}Mo_{0.1}O_y, where the ammonium vanadate, tungstate and molybdate were used and Ce_{0.9}Y_{0.1}O_y and Ce_{0.9}Sn_{0.1}O_y where YCl₃ and SnCl₂ were used. The order of experiments was randomised to minimise systematic error.

Parallel synthesis of doped cerium oxides. Cerium nitrate hydrate and the doping metal precursor were placed in ceramic vessels in an oven under reduced pressure. The molten precursors were left to boil overnight and then calcined in air for 5 h at 700 °C. *Example:* Ce_{0.9}Bi_{0.1}O₂. Cerium nitrate hexahydrate (3.784 g) and Bi(NO₃)₃·5H₂O (0.423 g) were placed in a ceramic vessel in an oven at 110 °C. The pressure was reduced to 20 torr over 15 minutes. The sample was left in the vacuum oven overnight, to obtain *ca.* 4 g of a sponge-like solid. The sample was calcined in air for 5 hours at 700 °C (ramp rate 300 °Ch⁻¹). The sponge-like structure remained intact after calcination, but was very delicate and easily crushed to a powder. As shown in figure S1, powder XR diffraction measurements of the various solid oxygen

reservoirs confirmed that the original fluorite structure was retained when 10% of the Ce ions were substituted.¹

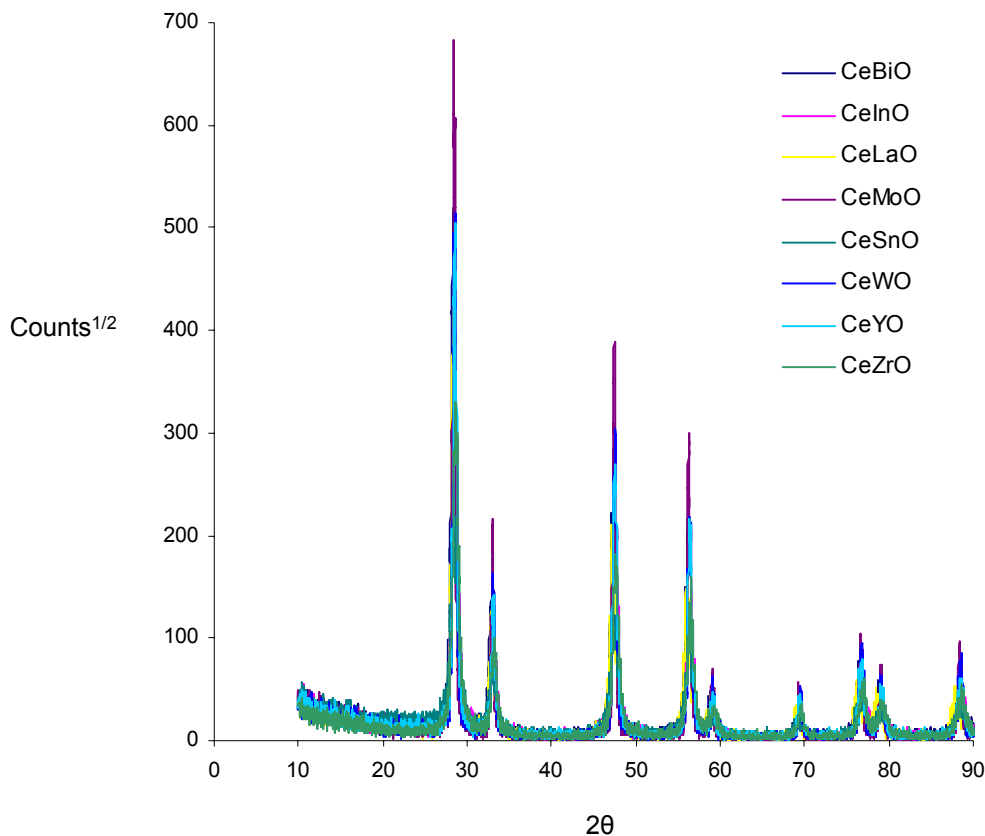


Figure S1. Powder XRD diffraction patterns for various oxygen reservoirs.

General procedure for cyclic redox experiments. The catalyst sample (50 mg) was mounted on quartz wool in a quartz tube reactor (3 mm inner diameter) and heated to 600 °C under He (50 mLmin⁻¹). The reactor temperature was maintained at 600 °C and the sample was subjected to a constant flow of 50 mLmin⁻¹ of 1% v/v O₂ in He for 18 min. The reactor was then purged with pure He for 1 min, subjected to a reducing mixture of 5% H₂, 20% C₂H₆ and 20% C₂H₄ (v/v in He) for 10 min, and purged again with pure He for 1 min. The product streams were analyzed by gas chromatography and selective mass spectrometry, enabling the separation and quantification of H₂, N₂, O₂, CO, CH₄, C₂H₄, C₂H₆ and CO₂, in this order.

[1] Doping at such low fractions, *i.e.* up to 10 mol%, causes only negligible to minor shifts in the peaks, see a) G. Colon, M. Pijolat, F. Valdivieso, H. Vidal, J. Kaspar, E. Finocchio, M. Daturi, C. Binet, J. C. Lavalley, R. T. Baker, S. Bernal, *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 3717. b) A. E. C. Palmqvist, E. M. Johansson, S. G. Jaras, M. Muhammed, *Catal. Lett.* **1998**, *56*, 69. c) Y. Zhang, S. Andersson, M. Muhammed, *Appl. Catal. B-Environ.* **1995**, *6*, 325.

The oxygen exchange, in mol kg^{-1} , was determined by subtracting the CO and CO₂ production from the total O₂ consumption in the oxidation step. This oxygen consumption has been measured using a trace of argon in the oxygen flow, monitored at every time step by following the Ar and O₂ MS-signals. The amounts of CO and CO₂ produced were calculated using both GC- and MS-measurements.