In-situ measurement of oxygen release from Ag/$SrFeO_{3-\delta}$ materials for chemical looping catalysis

A.R.P. Harrison[1], S.M. Fairclough[2], E.A. Willneff[3], A. Britton[3], E.J. Marek[1]*

1 Department of Chemical Engineering and Biotechnology, University of Cambridge, Philippa Fawcett Drive, Cambridge, UK; 2 Department of Materials Science and Metallurgy, University of Cambridge, 27 Charles Babbage Road, Cambridge; 3 School of Design, University of Leeds, 211 Clarendon Road, Leeds, UK

**Corresponding author: arph2@cam.ac.uk*

Highlights

- Reduction of Ag/$SrFeO_{3-\delta}$ measured using TEM-EELS and NAP-XPS at elevated temperature (400-700°C).
- Reduction of bulk $SrFeO_{3-\delta}$ occurs throughout the sample and is not localised near Ag.
- Presence of Ag results in formation of transient Ag-O species at the cost of surface O.

1. Introduction

Chemical looping selective oxidation offers a promising alternative to conventional oxidation catalysis. In chemical looping catalysis, a hydrocarbon stream is fed over a reactive metal oxide (termed an oxygen carrier, OC, *e.g.* $SrFeO_{3-\delta}$) impregnated with a metal catalyst (*e.g.* Ag). Lattice oxygen is transferred from the OC to the active site of the catalyst to react with the hydrocarbon and form the desired product. The feed is then switched to air to regenerate the OC and close the chemical loop, giving the safety advantage of inherent separation between the hydrocarbon and gaseous oxygen. Recent work [1] has shown that in addition to catalysing oxidation reactions, Ag increases the rate of oxygen release and reuptake from $SrFeO_{3-\delta}$ at low temperatures (≤400°C). However, the role of Ag in enhancing the rate of oxygen transport is poorly understood. Here, to elucidate the interactions between $SrFeO_{3-\delta}$ and Ag, we apply *in-situ* TEM and NAP-XPS and investigate the behaviour of Ag/$SrFeO_{3-\delta}$ during redox.

2. Methods

Strontium ferrite ($SrFeO_{3-\delta}$) was produced by solid state synthesis from stoichiometric amounts of $SrCO_3$ (Sigma Aldrich, >98%) and Fe_2O_3 (Honeywell Fluka, >99%), followed by calcination at 1000°C for 12 h, then sieved to 180-355 µm. Samples of $SrFeO_3$ were impregnated with $AgNO_3$ solution, then dried, and calcined for 5 h at 650°C, with target loading 15wt% Ag (designated Ag/$SrFeO_{3-\delta}$).

Transmission electron microscopy (TEM) was performed using a Thermo Fisher Scientific Spectra 300 operating at 300 kV with energy dispersive X-ray spectra (EDS) and electron energy loss spectra (EELS) collected in parallel. Powder samples were suspended in $CHCl_3$ (Sigma Aldrich, >99%), deposited onto a heating chip (DENSSolutions Wildfire), and inserted into the TEM. Near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) was performed using a SPECS EnviroESCA, with pelletised samples placed on an electrically heated stage, and sample chamber atmosphere set to 0.25 mbar H_2 or 1 mbar O_2 by supplying 5% H_2 in N_2 or synthetic air (all gases BOC). Scans of the O1s region were collected and calibrated with respect to the adventitious carbon C1s peak at 248.8 eV.

3. Results and discussion

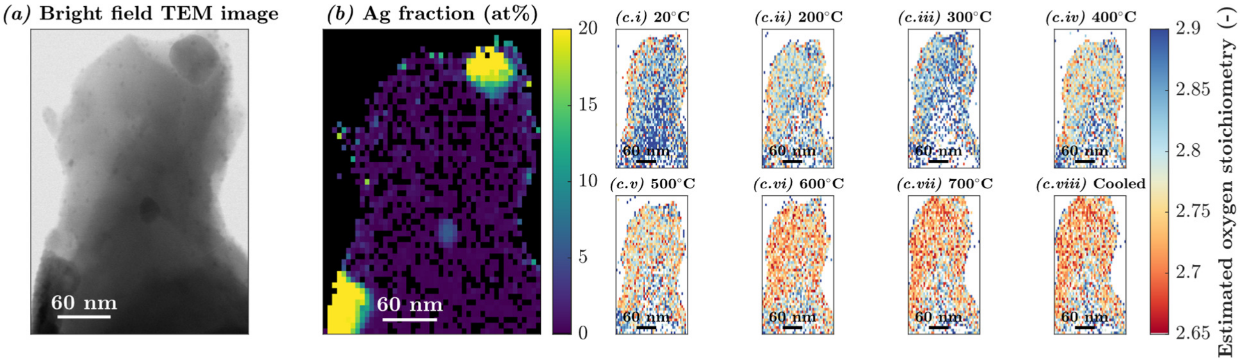

Figure 1. *In-situ* TEM of Ag/$SrFeO_{3-\delta}$, EDS map indicating Ag distribution, and EELS maps showing local oxidation state.

In-situ TEM measurements of a thin section of Ag/$SrFeO_{3-\delta}$ are shown in Fig. 1. At each point within the sample, EELS was applied to estimate the local Fe^{4+}/Fe^{3+} ratio, and hence, the oxidation state. Upon heating from 20°C to 700°C, the material became reduced, with a reaction front moving inwards from the edge of the sample. Reduced regions of Ag/$SrFeO_{3-\delta}$ were not localised around particles of Ag, suggesting rapid transport of O^{2-} ions within the $SrFeO_3$ lattice.

From NAP-XPS scans of $SrFeO_{3-\delta}$ at room temperature (shown in Fig. 2a), four distinct O species were detected: $SrFeO_3$-lattice O, SrO-lattice termination O, surface-O species, and impurities (-CO_3, -OH, *etc.*). The spectrum for Ag/$SrFeO_3$ showed an additional peak at intermediate binding energy between SrO and surface O, ascribed to transient Ag-O species (Fig. 2d).

Upon heating in 0.25 mbar H_2, surface-O species were removed from $SrFeO_{3-\delta}$ at T above 360ºC, whereas, for Ag/$SrFeO_{3-\delta}$, its Ag-O species started desorbing at ~180°C, followed by surface-O from $SrFeO_3$ above 300°C (Figs. 2g and 2i). At ~430°C (Figs. 2b and 2e), Ag/$SrFeO_{3-\delta}$ showed a lower fraction of surface-O than $SrFeO_{3-\delta}$ (11.5% *vs* 28.3%), suggesting that Ag aidd the removal of oxygen from $SrFeO_3$. Both samples also show a shift of ~+1.5 eV in the binding energy of $SrFeO_3$ lattice oxygen, corresponding to a change in Fermi energy for the reduced oxide [2]. When the gas was switched from H_2 to 1 mbar O_2, surface-O species rapidly re-formed on both samples (Figs. 2c and 2f), and remained stable throughout cooling to room temperature (Figs. 2h and 2j), whereas to Ag-O species in Ag/$SrFeO_{3-\delta}$, which continue to recover slowly during cooling.

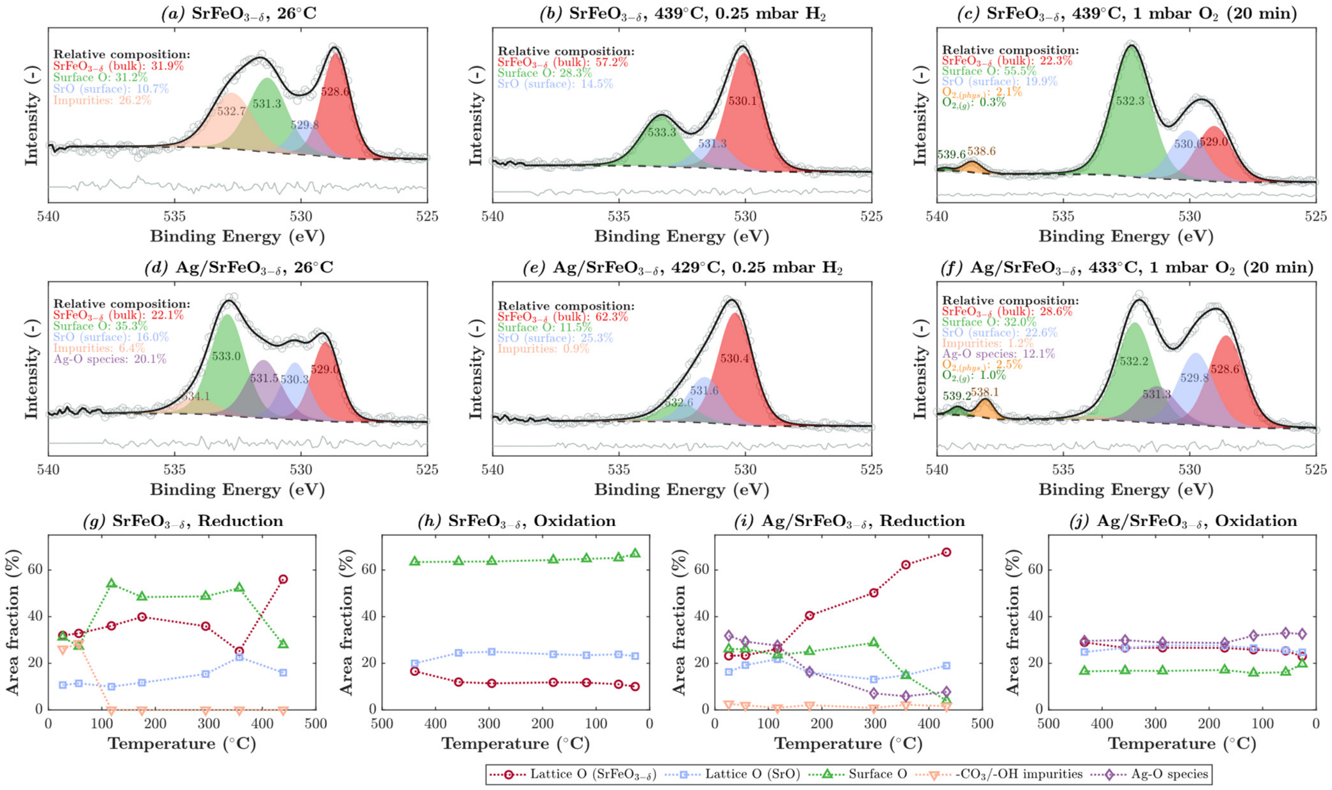

Figure 2. NAP-XPS O1s spectra of $SrFeO_{3-\delta}$ and Ag/$SrFeO_{3-\delta}$ under 0.25 mbar H_2 and 1 mbar O_2, showing changes in O species.

4. Conclusions

Oxygen release from Ag/$SrFeO_{3-\delta}$ is likely limited by surface reactions of Ag-O species, with little spatial variation observed within the sample during *in-situ* reduction, suggesting fast ionic transport in $SrFeO_{3-\delta}$. The Ag-O species on Ag/$SrFeO_{3-\delta}$ also accelerate the rate of $SrFeO_{3-\delta}$ regeneration.

References

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[2] A. Nenning *et al.*, *J. Phys. Chem. C*, 120, 3, (2016), 1461–1471,

Keywords

Chemical looping; perovskites; *in-situ* TEM; NAP-XPS